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DEVELOPMENT OF AN ANALYTICAL METHOD TO DETERMINE AROMATICS IN HEATING OILS AND DIESEL FUELS

Final Report

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EXECUTIVE SUMMARY

A method employing supercritical fluid chromatography (SFC) with flame ionization detection (FID) was developed for the determination of the aromatics content in heating oils and diesel fuels. Separation between saturates and aromatics was accomplished on a packed silica column with supercritical carbon dioxide as the carrier fluid. The best separation was obtained at 35°C and 3600 psi (24,800 kPa). In contrast to the fluorescent indicator adsorption (FIA) technique, the present method appears to be applicable to samples with final boiling points of up to 450°C and is not restricted by sample color. The analysis time by SFC is approximately 15 min. Because of the similar response of the FID to both saturates and aromatics fractions, it is assumed that the integrated area percentages may be used directly to determine the aromatics content without the need for extensive calibrations. However, non-linearity at higher concentrations does require that samples be diluted before analysis. It was not possible to calculate a sample recovery for analysis by SFC presumably because of poor injector repeatability, but this has no effect on the actual aromatics determination.

The repeatability by both SFC and FIA methods over the range of aromatics values of 20 to 80 wt% may be stated as follows, "duplicate measurements by the same operator should be suspect if they differ by more than 1 wt% 19 times out of 20". There is a strong correlation between the results obtained by both methods. Good correlations were also found between the results obtained by SFC and nuclear magnetic resonance, and by SFC and gas chromatography - mass spectrometry. The equipment required by SFC is more costly than that for FIA; however, it is fairly simple and reliable and it has been shown that a technologist may be easily trained in its use. Therefore, it is suggested that the SFC could be used in place of FIA in refinery control laboratories.

The potential exits for the determination of the mono-, di- and polyaromatic contents in middle distillate fuels by the SFC method. Because of the lack of pressure control and the overlap of aromatic types using the present system, this analysis is not applicable to all samples. Improvements may be expected with the installation of pressure control and a column switching technique.

SOMMAIRE EXECUTIF

Une méthode utilisant la chromatographie supercritique (SFC) et un détecteur à ionisation de flamme (FID) a été développée pour la quantification des aromatiques dans les huiles à chauffage et les carburants diesel. La séparation des saturés et des aromatiques a été effectuée sur une colonne à garnissage de gel de silice en utilisant le dioxyde de carbone sous conditions supercritiques comme phase mobile. La meilleure séparation a été obtenue à 35°C et 3600 psi (24,800 kPa). Par opposition à la méthode par adsorption en présence d'indicateurs fluorescents (FIA), la présente méthode n'est pas limitée par la couleur de l'échantillon et permet d'analyser des échantillons dont le point d'ébullition final peut aller jusqu'à 450°C. Le temps d'analyse est d'environ 15 minutes. Puisque la réponse du détecteur FID est similaire pour les saturés et les aromatiques, les pourcentages calculés à partir de l'aire sous les pics sont utilisés directement pour déterminer les concentrations en aromatiques. Cependant, comme la relation n'est pas linéaire à haute concentration, il est nécessaire de diluer l'échantillon avant analyse. Il n'a pas été possible de calculer le taux de récupération pour l'analyse SFC présumément à cause de la faible répétabilité de l'injecteur mais ceci n'a toutefois aucun effet sur la détermination des aromatiques.

La répétabilité des méthodes SFC et FIA pour des concentrations en aromatiques allant de 20 à 80% peut être définie comme suit: "Les mesures en duplicate effectuées par le même opérateur sont suspectes si elles diffèrent de plus de 1% 19 fois sur 20". Il existe une forte corrélation entre les résultats obtenus par les deux méthodes. De bonnes corrélations ont également été observées entre les résultats obtenus par SFC et résonance magnétique nucléaire (RMN), et entre la SFC et la chromatographie en phase gazeuse couplée à la spectrométrie de masse (GC/MS). L'équipement requis pour l'analyse SFC est plus coûteux que pour la méthode FIA; cependant, il s'agit d'appareillage assez simple et fiable, et facilement assimilable par un technicien. Il est donc suggéré que la méthode SFC remplace la méthode FIA dans les laboratoires de contrôle des raffineries.

La méthode SFC est potentiellement applicable à la détermination des composés mono-, di- et polyaromatiques. Mais à cause d'un manque de contrôle de la pression (programmation) et du recouvrement entre les sous-classes aromatiques obtenu avec le système actuel, l'analyse n'est pas applicable à tous les échantillons. Des améliorations seraient possibles avec l'utilisation d'un contrôle de pression et de la technique de commutation des colonnes.

INTRODUCTION

Background

The presence of high quantities of aromatic compounds in middle distillate oils causes problems for refiners and users because of the sooting propensity of such oils. Distillate fuels containing a high proportion of aromatic compounds are being produced due to the increased use of non-conventional crudes and the use of lower cost blending components to maximize product yield.

The method normally used in refineries for determining aromatics in oils is ASTM D 1319, the fluorescent indicator adsorption (FIA) method. FIA has poor accuracy and precision, and is limited to samples which are colorless and which have final boiling points below 315°C. Many methods based on high performance liquid chromatography (HPLC) are available, but most utilize selective detectors which require extensive calibration. Thin layer chromatography with flame ionization detection (TLC/FID) is also a possibility, but is limited to the higher boiling samples. Mass spectrometry (MS) and nuclear magnetic resonance (NMR) may also be used, but both require expensive instrumentation and highly trained operators.

There is a need for a simple, inexpensive but accurate method suitable for refinery use to determine total aromatics content in middle distillates. The method should be able to be instituted by existing refinery personnel, and should be applicable to samples with final boiling points up to 380 to 400°C. Furthermore, the determination of specific aromatic types, such as a classification according to the number of aromatic rings, would provide additional valuable information to be used in correlations with combustion studies.

Objectives

The principal objective of this work was to develop a method for determining the total aromatics content of heating oils and diesel fuels. The method was required to be superior to the FIA method in terms of accuracy, precision and analysis time, and to be suitable for refinery control laboratories where operators do not have skills in chemical analysis using sophisticated instrumentation. The method was intended for use with middle distillate fractions boiling between 150 and 380°C and possibly up to a final boiling point of 400°C.

A secondary objective was to extend this method to the determination of the mono-, di- and polyaromatic contents in heating oils and diesel fuels. This method would be used for research purposes to facilitate the development of correlations of combustion characteristics with aromatic types. At the present time it is not anticipated that it would be required in refinery control laboratories.

Review of Methods for Aromatics Analysis

A. Fluorescent Indicator Adsorption (ASTM D 1319):
The FIA method (1) has been used by the petroleum industry since its development by Conrad (2) and Criddle and LeTourneau (3) for the determination of saturates, olefins and aromatics in gasoline and jet fuel. The sample is separated, along with added fluorescent dyes, on a column of silica gel using isopropyl alcohol as eluent. The dyes leave the saturates colorless, the olefins yellow, the aromatics blue and the solvent front red. The volume percent of each hydrocarbon type is calculated by measuring the length of each colored zone.

The method depends upon the operator's ability to distinguish between the colored bands, which can be difficult for colored samples. It has been shown that certain cracked stocks yield poor separation of olefins and aromatics leading to erroneous results (4). The scope of the method excludes samples with final boiling points greater than 315°C, which is a severe limitation. It has been noted that problems have arisen with variations in dye composition and with availability of the proper grade and activity of silica gel (5). It has also been shown by MS of FIA separated fractions that there is overlap between component types (6). According to the ASTM definition of repeatability, duplicate results by the same operator should be considered suspect if they differ by more than 1.0 to 1.2 vol% (over the range of 20 to 80 vol% aromatics) 19 times out of 20 (1).

B. Nuclear Magnetic Resonance:
Both proton and carbon-13 nuclear magnetic resonance (NMR) are useful in determining not only aromaticities but also the structures of petroleum fractions, coal liquids and shale oils. The definition of aromaticity by ^{13}C NMR is the percentage carbon in aromatic rings or the ratio of aromatic carbons to total carbons (7). Petrakis et al (8) have discussed three basic approaches which have been used to obtain structural information. The first is characterization by structural parameters which describe such features as fraction of carbon that is aromatic, the number and length of alkyl substituents in an average molecule and the average number of aromatic rings per molecule (9-11). Repeatabilities for the aromatic carbon analysis have been reported to be on the order of 5% relative standard deviation (RSD) (11). The second approach utilizes NMR, elemental composition and average molecular weight data to construct average molecular structures (12). The final approach uses elemental analysis, NMR and other analytical data to determine functional group concentrations (8).

In contrast to other methods of hydrocarbon type analysis, carbon-13 (or proton) NMR data provide the percentage distribution of aliphatic and aromatic carbon (or hydrogen) atoms in the sample (6). Chromatographic and MS methods provide weight percentages of saturate and aromatic molecular types; the former based on an actual molecular separation, the latter on molecular fragmentation patterns. Because of these differences, NMR data may be correlated to that of other methods in order to obtain useful information, for example on the "average" number of carbons in the alkyl side chains attached to the aromatic rings.

C. Mass Spectrometry:
Analysis of crudes and petroleum fractions by MS have proven to be of great value in the understanding of compositional problems in petroleum processing (13). There are two commonly used MS group-type analyses employed to obtain quantitative information. One is the Robinson-Cook (14) method for analysis of the aromatics fractions; the other is the group-type analysis for the saturates fraction (15). These group-types can include the breakdown of saturates into alkanes and 1 to 6-ring cycloalkanes, and of aromatics into mono- to penta-aromatics and aromatic sulfur species.

These MS methods can be applied with good precision only to samples which are low in olefins and heteroatoms (S, N, O) (6). These classes of compounds are a source of interference in the calculations based on the spectral information. Absolute comparison of group-type concentrations obtained by chromatographic and MS analysis should not be attempted (13). Since the MS analysis is based on fragmentation patterns, a true distinction of every parent molecule in a mixture cannot be made.

D. High Performance Liquid Chromatography:
Many HPLC methods have been employed for saturates and aromatics determination. Generally these methods are characterized by good separation, analysis times of less than 10 minutes, and are not limited to low boiling samples. Their main disadvantage is the specificity of the usual ultraviolet (UV) and refractive index (RI) detectors, which require extensive calibration using either model compounds similar to those in the samples being analyzed, or fractions prepared from the actual samples by open column chromatography.

Suatoni and Swab (16) used a μ-Porasil column with n-hexane mobile phase to determine saturates, aromatics (which were backflushed) and polar compounds (which were retained on the column and determined by difference). Detection was by RI. Repeatabilities varied from 0.5 to 7% RSD. Alfredson (17) used a cyanopropyl column coupled to a silica gel column to separate saturates, olefins, aromatics and polars. Mobile phase was n-hexane, and detection was by UV and RI. Wise et al (18) found that HPLC with a stationary phase of amino-modified silica and n-hexane as mobile phase provided good separation of aromatics according to number of rings. Grizzle and Sablotny (19) found that a semi-preparative HPLC method using amino-modified silica required two columns in series to completely resolve the saturates and monoaromatics. They also stated that differences exist among commercially available stationary phases even in columns containing the same absorbent. Cookson et al (20) used a bonded aminosilane stationary phase, n-heptane mobile phase and RI detection for quantitation of saturates, mono-, di- and polyaromatics, and polars of olefin-free kerosine and diesel fuels.

Two detectors thought to be preferable to the RI and UV, because of their relative uniformity of response for hydrocarbon types over a wide range of carbon numbers, are the dielectric constant (DC) detector and the flame ionization detector (FID). This uniformity of response greatly simplifies the calibration procedure. Hayes and Anderson (21) used a DC detector in conjunction with conventional HPLC employing Partisil columns and n-butylchloride as the mobile phase to determine saturates, monoaromatics and polyaromatics in fuel distillates. Repeatabilities were in the range of 1%

RSD, and accuracy estimated to be within 2% absolute. The FID presents a problem when used with conventional HPLC because of interference from commonly used solvents. Norris and Rawdon (5) have successfully coupled supercritical fluid chromatography (SFC) with FID employing carbon dioxide as the mobile phase. This will be discussed in the next section.

TLC/FID has also been used for component type analysis, although it is limited to samples with boiling points above about 250°C (22,23). It has been shown that premature evaporation of the lower boiling material occurs in the FID (24). Because of this limitation the method is considered unsuitable for middle distillates.

E. Supercritical Fluid Chromatography with Flame Ionization Detection:
SFC is chromatography in which the mobile phase is a supercritical fluid which has properties intermediate to those of a gas and a liquid (25). This condition is achieved with an operating temperature and pressure higher than the critical temperature and pressure of the mobile phase. Under such conditions the diffusivity is higher in a supercritical fluid compared to a liquid, resulting in increased resolution and decreased analysis time for SFC compared to liquid chromatography. Another advantage of SFC is that as the density of the fluid is increased by raising the pressure, progressively higher molecular weight and thermally labile compounds may be analyzed which cannot be handled by gas chromatography. Even though increasing the pressure results in a loss of selectivity within a homologous series, group-type separation remains good. This can be advantageous when class separations (saturates, aromatics) are desired in wide molecular weight ranges.

The usefulness of the FID, namely its relatively consistent response for different hydrocarbon types, can be used to advantage when coupled to SFC since it is easy to accomplish solute desolvation, and certain supercritical fluids such as carbon dioxide yield low background signals (26). One problem that has been observed, however, is detector "spiking" caused by rapid desolvation of solute molecules and the formation of aggregates (27). This effect can be reduced by adjusting the restrictor size to smooth the transition of the solute molecules into the flame.

Norris and Rawdon (5) used SFC with a modified FID to determine saturates, olefins and aromatics in petroleum liquids. They employed a carbon dioxide mobile phase at 35°C and 2600 psi (18,000 kPa) and columns of 5μ silica and RoSil-5 coated with silver nitrate. Each sample analysis was completed in an average of 5 min. Repeatabilities ranged from 2 to 6% RSD. Direct comparison of the SFC results obtained for gasoline range samples with FIA analysis could not be carried out because the former are reported in wt% whereas the latter are given in vol%. The same trends, however, were observed for both sets of data. The correlation coefficient was 0.988. With this method the potential also exists for the further classification of aromatics by ring number.

Schwartz and Brownlee (28) have also recently employed SFC to determine paraffins, olefins and aromatics in gasolines. They used a silica microbore (1 mm ID) column with sulfur hexafluoride as the mobile phase to separate the paraffins and olefins at 50 °C and 3400 psi (23,400 kPa). Aromatics were

eluted by a step-program of pressure, flow and temperature. Repeatabilities on area % measurements for replicate injections of a mixture of standard compounds ranged from 0.4 to 0.9% RSD.

Campbell and Lee (29) obtained good separation between aromatic types using a semi-preparative SFC method with CO_2 and an amino-modified silica stationary phase. In the SFC work of Lundanes and Greibrokk (30) a silver nitrate treated silica column provided complete separation between saturates and aromatics which was not obtained using a silica column alone. Wright et al (31) have reported on the coupling of capillary column chromatography with MS for the characterization of complex fuel and environmental samples.

The method proposed for the present study was based on the work of Norris and Rawdon (5). The main reasons for its selection were as follows: short analysis time, relatively low cost instrumentation, minimal amount of operator training required, little or no sample preparation, and the possibility that calibration would not be required. It was felt that the HPLC-DC method of Hayes and Anderson (21) required somewhat less common equipment and longer analysis times.

EXPERIMENTAL

Equipment and Materials

A schematic of the SFC/FID set-up is shown in Figure 1A and a photograph in Figure 1B. The major components are described separately below.

A. Refrigerated circulator bath:
A Lauda model K4R circulator bath was used in the earlier work reported here (shown in Figure 1A) to keep the 250 mL syringe pump cooled while filling it with liquid carbon dioxide. The circulator was capable of controlling the temperature of the fluid, which consisted of 70 % water and 30 % methanol, at 5°C.

Carbon dioxide cylinder equipped with a helium headspace (alternative to above):
A carbon dioxide cylinder prepressurized to 1200 psi (8270 kPa) with helium which has been described by Schwartz (32) was used in the later work reported here. This allowed the filling of the syringe pump with CO_2 without cooling thereby reducing the cost of equipment required.

B. Syringe pump:
A Varian model 8500 pump was used to regulate the pressure of the carbon dioxide through the chromatographic column. It had a capacity of 250 mL and was capable of delivering flow rates from 1 to 100 mL/hr. A valve was installed on the fill line at the pump, so as to isolate the CO_2 cylinder from the syringe pump when filling and delivering CO_2 under pressure.

C. Pressure relief valve:
A three-way valve, SSI model 02-126 with 1/8 in. (3.18 mm) fittings or model 02-0125 with 1/16 in. (1.59 mm) fittings, was installed after the pump to provide a mechanism to vent off the carbon dioxide in the system for the purpose of changing columns or repairing injectors.

D. Pressure gauge:
The pressure was monitored with a 6 in. (152 mm) diameter Marsh gauge model D33990BZ, 0 to 10,000 psig (68,900 kPa) with markings every 50 psig (345 kPa).

E. Sampling valve:
A Rheodyne valve model 7520 equipped with a 0.2 μL internal sample loop mounted on the exterior of the gas chromatograph was used to introduce the sample onto the column.

F. Gas chromatographic oven:
A Shimadzu model GC-8A gas chromatographic oven was employed in which a 1/16 in. (1.59 mm) tubing was connected between the injector and the chromatographic column. The oven was run isothermally and was equipped with an FID.

G. Chromatographic columns:
All columns were 250mm x 2.1mm ID (Alltech Associates). The following stationary phases were employed: 5μ silica adsorbosphere, 5μ cyano, 5μ amino, and 20% $AgNO_3$ on 5μ silica. It was necessary to place the columns diagonally across the oven compartment so as to avoid having to bend them.

H. Restrictors:
The restrictors were flexible fused silica capillary tubing attached to the column with a 0.4mm 40% graphite ferrule with a low dead volume fitting. Either 50mm of 10μ ID tubing inserted approximately 30mm into the FID, or 130mm of 20μ ID tubing inserted approximately 90mm into the FID, as close as possible to the flame, was used. The former arrangement is shown in Figure 2. The latter arrangement was found to eliminate "spiking", a common problem in SFC (27).

I. Integrator:
A Spectra Physics model 4290 computing integrator was used for the collection and reduction of the data.

J. Miscellaneous equipment and materials:

- 1,2,5,and 10 mL volumetric flasks.
- 100 and 250 μL gas tight Hamilton type "RN" syringes.
- 1/16 in. (1.59 mm) OD X 0.004 in. (0.1 mm) ID stainless steel tubing.
- The following gas regulators for the hydrogen, air and helium cylinders:
  compressed air regulated at 37 psig (255 kPa).
  compressed hydrogen (prepurified) regulated at 42 psig (290 kPa).
  compressed helium regulated at 45 psig (310 kPa) to control valves on the Model 8500 Varian syringe pumps.
  compressed carbon dioxide, equipped with siphon or eductor tube (as above, can be equipped with helium headspace as alternative to the refrigerated bath).
- An in-line filter to remove water from the liquid carbon dioxide before it enters the syringe pumps. A suitable unit was purchased from Matheson Gas Products, a model 450 used in conjunction with a model 452 cartridge.
- Fisher Scientific ACS grade carbon disulfide (CS_2) (catalog no. C-184B) was used without further purification for all of our work.
- All other chemicals used were 99 mole % grade or better.

Samples

The diesel and middle distillate samples were provided by: the Scientific Authority, the Gasoline & Oil Testing Laboratory at the Alberta Research Council, and Imperial Oil Strathcona Refinery.

Operating Procedure

A. The GC was turned on. If a refrigerated circulator bath was used it was turned on and allowed to equilibrate for at least 30 min. Once the syringe pump reservoir had cooled down sufficiently the valve on the carbon dioxide

cylinder and the one-way valve were opened to fill the pump with liquid CO_2. If a carbon dioxide cylinder prepressurized with He was used, the pump was completely filled at ambient temperature by opening the two previously mentioned valves. The one-way valve was then closed to prevent CO_2 from pumping back into the tank, and the fast pump button pressed to bring the pressure of the system quickly up to the operating pressure of 3600 psi (24,800 kPa). It was found that slight adjustments to the pressure were required initially, until the system stabilized.

B. The FID temperature was set at 400° C, and the flow rates were adjusted as follows: air at 300 mL/min, and hydrogen at 40 mL/min. the detector was then ignited and the instrument allowed to operate for about 10 min. before proceeding.

C. The syringe pump flow rate was set at 8 mL/hr of liquid CO_2 and the GC oven temperature was set at 35° C.

D. The sample was diluted (1:10 by volume) in CS_2. Approximately 10μL of diluted sample were introduced into the injection valve using a 100μL syringe. With the syringe in place, the valve was switched from the "load" position to the "inject" position and the recording/integrating device started immediately. The injection valve was left in the "inject" position until the completion of the run.

E. The chromatogram was allowed to develop until the last peak had returned to baseline. Since most peaks had eluted by 15 min., our integrator was set to automatically terminate after this length of time. At the completion of the run the integrator would report the actual area counts for each peak as well as the retention time and the normalized area percents. If the samples had been diluted with CS_2 the reported normalized area percents would have to be recalculated taking the area of the CS_2 impurity peaks into account.

F. Calculations

If the CS_2 impurity peak had been separately integrated:

$$\text{wt \% aromatics} = A_a\% \times [100/(100-A_c\%)] \quad (1)$$

where $A_a\%$ = area % of aromatics peak
$A_c\%$ = area % of CS_2 impurity peak

If the CS_2 impurity peak fell under the saturates peak:

$$\text{wt \% aromatics} = A_a\% \times [A_t/(A_t-A_c)] \quad (2)$$

where A_t = total area
A_c = area of CS_2 impurity peak (obtained from a blank solvent run)

G. Safety Considerations

CS_2 - highly toxic by inhalation and skin absorption. Extremely flammable. High explosion hazard.

A summary of this procedure is given in the flowchart in Figure 3.

Preparation of Saturates and Aromatics Fractions

A modification of the column chromatographic procedure of Sawatzky et al (33) was used for the preparation of saturates and aromatics fractions from several actual samples. A 1 mL stainless steel sample loop was connected through a sampling valve to the bottom of the column. The column consisted of 304 stainless steel tubing, 137cm x 0.94cm ID packed in its lower half with 37g (before activation) of Davison Grade 12 (28-200 B.S. mesh) silica gel acivated at 250°C for 20 h. The top half was packed with 47g (before activation) of Alcoa F-20 (30-200 B.S. mesh) alumina activated at 400°C for 20 h. A separatory funnel was connected to a Milton Roy mini-pump for delivering eluent to the bottom of the column through the sampling valve. The collection cylinder was set in an ice bath to keep evaporation to a minimum.

Two series of eluents were employed to separate samples into component type fractions. In the first, after loading 1 mL of sample through the loop, the saturates were eluted from the column with 250 mL of n-pentane and a total aromatics fraction with 500 mL of toluene. These fractions were carefully air-dried and then used for checking the FID response factors. In the second, the monoaromatics were eluted with 250 mL of 5% toluene in pentane, the diaromatics with 250mL of 15% toluene in pentane and the polyaromatics with 250 mL of toluene.

RESULTS AND DISCUSSION - TOTAL AROMATICS CONTENT

Saturates-Aromatics Separation

A. Effect of Temperature: Retention time data for a series of model compounds are shown in the first two columns of Table 1A for the silica stationary phase, mobile phase pressure of 3600 psi (24,800 kPa) and temperatures of 90 and 35°C. For ease of comparing different columns and conditions, these retention times have been converted to capacity factors which are shown in Table 1B. The capacity factor, k, is defined by:

$$k = (t_R - t_o) / t_o \qquad (3)$$

where t_R is the retention time of the given model compound, and t_o is the retention time of a compound not retained by the column which in this case is the impurity peak in the CS_2 solvent. The greater the difference in k values between the highest boiling saturate and the lowest boiling aromatic the better the saturates-aromatics separation. It can be seen that at both temperatures for the silica column, the saturates span a much smaller range of k values than do the aromatics. However, at 35°C the saturates as a group are better separated from the monoaromatics. For example at this temperature C_{30} has a lower k value than does benzene, but at 90°C, C_{20} and toluene have approximately the same k values. The boiling points of toluene and C_{30} correspond approximately with the lowest initial boiling point and the highest final boiling point of all middle distillate samples studied in the present work. The boiling point data as determined by gas chromatographic simulated distillation (ASTM D 2887) are shown in Appendix 1.

The dramatic improvement in saturates-aromatics separation upon decreasing the oven temperature is shown for an actual sample by the chromatograms in Figure 4. The sharp initial eluting peak is due to the saturates. At 35°C there is almost baseline separation between the saturates and the monoaromatic group of peaks. An added advantage of operating at the lower temperature is the shorter retention times, which would result in shorter analysis times per sample. For example as seen from Table 1A, phenanthrene elutes in 11.3 min. at 90°C compared to 6.1 min. at 35°C This can be attributed to increased density of the supercritical CO_2 at the lower temperature, which increases its solvating ability (25).

B. Effect of Pressure: Since the SFC system runs under flow control rather than pressure control, some day-to-day variation in the pressure was observed. As the study progressed, it was possible to reduce this variation (but not eliminate it) by noting the dependence of the final equilibrium pressure on the pump rate and fine tuning this rate accordingly.

There was some improvement in separation between saturates and aromatics at 90°C when the pressure was increased from 3250 to 3600 psi (23,400 to 24,800 kPa), as seen by the comparing the chromatograms in Appendices A3-16 and A5-16. At 3600 psi the monoaromatic peaks are just barely resolved, whereas at 3250 psi they are right under the broader saturates peak. This is presumably due to the increased density of the CO_2. At 35°C, however, which is just

above the critical temperature, there was virtually no change in the separation over the pressure range of 3000 and 4200 psi (20,600 and 28,900 kPa), as seen in Figure 5, even though there was an overall decrease in retention times.

C. Effect of Stationary Phase: Grizzle and Sablotny (19) reported from HPLC using an aminosilane stationary phase and hexane/methylene chloride mobile phase that good separation of saturates and aromatics, and of aromatics based on number of rings required the use of two columns. Lundanes and Greibrokk (30) reported that a silver-impregnated silica column was required to obtain complete separation of saturates and aromatics by SFC using CO_2. Based on these studies we investigated three other columns or combinations in an attempt to improve upon the separation between saturates and aromatics.

The data obtained at a pressure of 3600 psi (24,800 kPa) and temperature of 35°C are shown in Table 1B. It can be seen that the separation using the silica/cyano (Si/CN) combination is not quite as good as that of the silica at the same temperature; C_{30} and xylene have the same k value with the former, whereas C_{30} has a smaller k value than xylene for the latter. For the amino (NH_2) column the separation between saturates and aromatics is much poorer as seen from Table 1B; in this case C_{30} has the same k value as hexamethylbenzene. From the limited number of compounds run, it appears from Table 1 that a silica column followed by a 20% $AgNO_3$ on silica column (Si/Ag) is no better than silica at 90°C.

This comparison among stationary phases is made clearer by the SFC chromatograms for an actual sample shown in Figure 6. The monoaromatic group of peaks are seen to be best separated from the saturates using the Si column. This group type separation gets worse in going from the Si/CN to the NH_2 column. As will be mentioned later, in contrast to the above effect, the separation between mono- and diaromatics gets better as we proceed from the Si to Si/CN to NH_2 columns.

It is concluded that of the stationary phases studied in our SFC system, the best saturates-aromatics separation is obtained using a 5μ silica column. A discussion of the separation of aromatics according to number of rings for which different stationary phases might be advantageous will be made later.

Calibration of Saturates and Aromatics

In order to check the implicit assumption made by Norris and Rawdon (5), that the FID response factors for saturates and aromatics are the same, some calibration studies were carried out. We also wished to investigate whether the calibration curves departed from linearity at high concentrations, since this would place limits on the ranges in which quantitative data could be obtained. The calibration curves were determined using saturates and aromatics fractions prepared from actual samples, and compared to those obtained using several pure compounds.

Fractions were prepared from the following samples: HAD, 284, 3256 and 102. The percentages of each fraction recovered are listed in Table 2. The values were all less than 100% because of evaporation of the light ends during the preparation of the fractions. As seen by the distillation data (ASTM D 2887, simulated distillation by GC) listed in Appendix 1, the poorest recovery was obtained from the sample (284) with the greatest amount of low boiling material. The SFC chromatograms obtained at 90°C and 3250 psi are shown in Figures 7 to 10. A high degree of purity is indicated which implies that the separations by column chromatography and SFC are similar which makes the fractions suitable for calibration purposes.

The calibration curves obtained at 90°C and 3250 psi over a broad range of concentration using CS_2 solutions of the saturates and aromatics fractions are shown in Figure 11. Curvature was noted for the saturates above approximately $100x10^6$ area counts. The likely reason for this behavior is that the FID becomes saturated above a certain concentration. The saturates which have a much sharper peak saturate the detector at a lower concentration than do the aromatics. Replotting only the linear region of each data set gave the results shown in Figures 12 and 13. The data points, which are listed in the lower portion of these figures, were fitted to the curve: $y = A * x$. It can be seen that the response factors as given by the slopes of each line differ by only 5%.

A comparison of the slopes of the saturates and aromatics fractions to those obtained with some pure compounds also at 90°C and 3250 psi is given in Figure 14. The data points for the pure compounds are given in Appendix 2. It was initially found that when hexane was run diluted in CS_2 the response factor was 20% lower than that of toluene. In this case the CS_2 impurity peak was directly underneath the hexane peak, and was likely interfering with the FID. When the hexane calibration was performed using dilution in methanol (which has a very long retention time and hence does not interfere) the response as shown in Figure 14 was obtained. All other compounds were prepared as CS_2 solutions.

It can be seen from Figure 14 that there are differences in the response factors of individual compounds similar to that reported in the GC/FID work of Dietz (34). Furthermore the low molecular weight model compounds, hexane and toluene, are unlikely to be present in middle distillate samples in significant amounts. The response factors determined for the saturates and aromatics fractions isolated from four actual samples presumably represent an average of the compounds contained in the samples. Since they differed by only 5%, it was decided that the integrated area %'s may be used directly to quantitate saturates and aromatics. Therefore, no routine calibration procedure should be necessary.

Dilution of Samples

Because of the non-linear saturates calibration curve at high concentrations noted above, it was necessary to reduce the concentration of sample reaching the FID. This was accomplished by dilution of the sample. The solvent CS_2, despite its known toxicity, was used because of its negligible response by the FID. There was, however, an impurity in this solvent which gave rise to a small peak either just ahead of or underneath the saturates peak. An example of this is the

first small peak in the chromatogram of sample HAD which is shown in Figure 7. All data were corrected for this impurity by the use of equations 1 and 2. Since the magnitude of this correction was less than 1 wt% purification of the CS_2 was not considered necessary.

In order to ensure that linearity was not a problem, the attenuation on the integrator was adjusted so that the peaks would be off-scale when the linear range was exceeded. As was stated earlier, peak height was the most likely criterion for saturation of the FID. Since the saturates give sharper and higher peaks than aromatics, the attenuation was set using the saturates calibration data. It was found for all samples in this study that a 1:10 by volume dilution was sufficient to bring the saturates into the linear range in which the calibration was carried out. It is recommended, however, that the attenuation be routinely set as just described so that the operator will be alerted to the fact that further dilution may be required.

Accuracy

The accuracy of the method could not be determined using actual samples since the absolute aromatics contents were not known. As already discussed in the Introduction section, other methods such as FIA, NMR, MS and HPLC are used for determining aromatics content but in general all of them define component types in somewhat different ways. Therefore, these methods will not be used to define the absolute aromatics content, but results obtained using these methods will be compared in a later section to the SFC results to see if the trends are similar.

The accuracy of the method was indicated using known mixtures of hexadecane and naphthalene in CS_2. The results are given in Table 3. Since the actual response factors for these two compounds were known to be different (see Figure 14), they were used in the calculations to determine absolute accuracy. The differences between measured and actual values ranged from 0 to 1 wt%.

Precision

The mean wt% aromatics values, standard deviations and relative standard deviations obtained from multiple analyses of 22 samples of diesels and middle distillates using a silica column under three sets of conditions are given in Table 4. All samples were diluted (1:10) in CS_2. Typical chromatograms of each sample under the three sets of SFC conditions are shown in Appendices 3, 5 and 7 (in the same order as given in Table 4); the corresponding results of the individual analyses are given in Appendices 4, 6 and 8. The arrows shown in each chromatogram in Appendix 7 indicate the saturates-aromatics cut points. Comparison with the chromatograms obtained at 90°C (Appendices 3 and 5) shows that for most samples, only at 35°C was there a definite valley between the initial sharp saturates peak and the first eluting monoaromatics peaks which made it obvious where to place the cut point. It was already mentioned that absolute retention times are not generally good indicators of the cut point because in the absence of pressure control in the current system the retention times vary somewhat from run to run.

The standard deviations in Table 4 do not increase as the mean value increases, but are scattered. Therefore, the repeatability statement is most logically quoted in terms of a standard deviation and not a relative standard deviation. The pooled standard deviations, s_{pooled}, were calculated from all the data using the following formula (35):

$$s_{pooled} = \sqrt{[\Sigma(n_i-1)(s_i)^2 / \Sigma(n_i-1)]} \qquad (4)$$

where n_i = no. of measurements on sample i
s_i = standard deviation from the mean

According to ASTM C 670-81 (36) the standard deviation is multiplied by the factor, $2\sqrt{2}$ or 2.83 to obtain the repeatability. This repeatability statement is as follows: "Duplicate measurements by the same operator should be considered suspect if they differ by more than (2.83 x s) 19 times out of 20".

The pooled standard deviations and repeatability statements for the data obtained under the three conditions are shown in Table 4. The best repeatabilities are generally observed under conditions which result in the best separation between saturates and aromatics. This is likely the result of the greater certainty in the cut point. A general trend toward higher aromatics values as the separation between saturates and aromatics improves is also observed from Table 4. One would expect that the more "correct" values are from the best separation conditions. We will comment more on this when comparisons to other methods are made.

The preceding precision studies were carried out by a technologist from Chemex with only one year of experience in a chemical laboratory performing GC analysis. Only about three days was required for this individual to become familiar with the operation of the instrument and to perform the analyses. This indicates the relative simplicity of the technique and suggests its suitability for use in refinery control laboratories.

The repeatability of the absolute area measurements obtained by repeated injection of the same samples was poorer than that of the relative areas (or wt% aromatics) determined above. The absolute area count measurements for multiple injections of three different samples are shown in Appendix 9. There is a large amount of scatter as indicated by the relative standard deviations, although if the points indicated by the asterisks (which could be bad injections) are excluded the scatter is reduced somewhat. It is thought that this scatter is the result of poor injector repeatability. Schwartz and Brownlee (28) also found in SFC work that better repeatability was obtainable from relative area measurements than from absolute area measurements. No explanation was given for this.

This poor repeatability does not however, affect the aromatics determination as is shown in Appendix 9 by the aromatics values for these particular samples. This is because the aromatics determination is based on relative values and does not depend upon the absolute amount of material injected, provided that concentrations are within the linear detector range of the saturates.

Sample Recovery

It was originally expected that a calculation of the sample recovery would allow not only a check to be made on the validity of the SFC results, but also a quantitation of the amount of polar material not removed from the column (which would be applicable to heavier samples). Since the exact sample loop size was not known (it was approximately 0.2 μL), the actual amount of sample injected could not be calculated. The recovery therefore was calculated by dividing the sum of the absolute saturates and aromatics concentrations (in CS_2) determined from the calibration curves, by the density of the sample. An example calculation is given in Appendix 10.

The results of recovery calculations for a number of dilutions of four of the samples are given in Table 5. Most of the mean values are within the 94 to 106% range; however, there is considerable scatter in these data as seen by the standard deviations. This scatter could be the result of poor repeatability of the injector as previously discussed. Whatever the reason, calculations of sample recoveries are unreliable.

One possibilty for solving this sample recovery problem would be to employ an internal standard method. This is recommended for future work.

Limitations of the Method

There are several limitations to the method, some of which can be avoided by care on the part of the operator. First of all, most samples cannot be injected neat, but must be diluted to bring all peaks into the linear range of the detector. This does introduce an extra step into the procedure and requires a small correction to be made in the calculations to account for the solvent impurity peak. Secondly, "spiking" was observed with some samples particularly with the higher boiling ones. Examples are samples 185 and ST-10 shown in Appendices A3-4 and A3-18 in which the "spikes" are indicated by arrows. As mentioned previously, this is suspected to be caused by rapid desolvation of the solute molecules and the formation of aggregates (27). This behavior is not so much a limitation as a nuisance since the integrator will detect each "spike" as a separate peak. The extent of the "spiking" does become more severe the higher the boiling range of the sample. In fact the worst samples were those which were 90% off at 370°C or higher. It has been suggested by Guthrie and Schwartz (37) that an integral restrictor positioned in the FID liner such that its end is even with the jet tip eliminates this "spiking". In the present work this positioning of a linear restrictor appeared to be sufficient to eliminate the "spiking" as evidenced by the chromatograms of samples 185 and ST-10 in Appendices A7-4 and A7-18. Finally, as already mentioned, the relatively poor repeatability of absolute area counts makes the calculation of sample recoveries unreliable. Such calculations would have made possible a check on the aromatics determination results, and also (for relatively high boiling samples) a quantitation of the amount of polar material not eluted from the column. It is recommended that an internal standard might solve this problem.

Comparison of Results by SFC/FID and Other Methods

A. FIA:

Despite its disadvantages, FIA is the most widely used standard method in the oil industry for aromatics determination. For this reason it was used as a basis for comparison of the present SFC/FID results. This comparison is shown by the plot in Figure 15. The SFC data were obtained under the conditions of optimum separation of the saturates and aromatics (35°C and 3600 psi); the FIA data were obtained according to the standard ASTM method (1). The two sets of data as well as the 90% off simulated distillation values from Appendix 1 are listed in Table 6. A linear regression of the data, indicated by the solid line in Figure 15, yielded a correlation coefficient of 0.9018. The 95% confidence interval for this regression is given by the dashed curves. The consistent bias, of all but three of the points, to higher values by SFC/FID (slope=0.97) could reflect the fact that the output of FIA is in vol% whereas that for SFC/FID is in wt%. This has also been indicated in the work of Norris and Rawdon (5).

Two possible explanations are given to explain why three of the points in Figure 15 are well outside of the confidence limits and give lower values by SFC/FID than by FIA. First, these three points represent samples (103, 185 and 3256) which yielded olefins values by FIA of greater than 3 vol% as seen from Table 6. By SFC olefins have retention times intermediate to saturates and monoaromatics using a silica column (38). In fact the chromatograms of these three samples do show significantly more overlap between saturates and monoaromatics than the other samples as seen from the corresponding chromatograms in Appendices A7-3, A7-4 and A7-9. Since the saturates peak is much sharper than that of the monoaromatics, the proportion of aromatics calculated as saturates would be larger than that of the saturates calculated as aromatics. This could result in a lower than expected value for aromatics by SFC. Secondly, two of these samples (103 and 185) possess 90% off values significantly greater than the 315°C theoretical limit for the FIA method, which may result in an error in these two vol% aromatics numbers.

B. NMR:

Since aromaticity measurement by NMR is a well established technique, the SFC/FID data were also compared to aromaticities which were provided by the Scientific Authority. The percentage aromatic carbon values were calculated from the ^{1}H NMR integral intensities according to the method reported by Muhl et al (39). The instrument used was a Varian EM-390 operated at 90 MHz. Samples were prepared by mixing approximately 50:50 by volume of sample with chloroform-d (99.99%) and adding a drop of tetramethylsilane as reference. The comparison of carbon aromaticities by NMR and wt% aromatics by SFC is shown in Table 7 and Figure 16. A linear regression of the data yielded a slope of 0.69 and a correlation coefficient of 0.8923.

Aromaticity as defined here is the percentage carbon in aromatic rings or the ratio of aromatic carbons to total carbons (7). Wt% aromatics by SFC/FID, on the other hand, refers to molecules containing at least one aromatic ring which in general will be substituted with alkyl side chains. Therefore, the SFC-NMR correlation indicates that "on average", 69% of the

carbon atoms in the aromatic molecules in these samples are contained in aromatic rings, with the remainder in alkyl side chains. Expressed in another way, the "average" substituted naphthalene molecule in these samples would contain between four and five carbons in alkyl side chains. The goodness of the SFC-NMR correlation, therefore, is not really an indication of the correctness of the SFC values, but rather provides information as to the amount of aromatic ring substitution.

Finally, it is interesting to note that the three samples which deviated from the SFC-FIA linear correlation (103, 185 and 3256) were well within the 95% confidence limits of the SFC-NMR correlation. As stated above this does not prove that the FIA values are incorrect, but it does place some confidence in the SFC values.

C. GC-MS/NMR:

The GC-MS spectra were recorded on a Finnigan Model 1020B quadrupole mass spectometer equipped with a standard electron impact source. Ionization was accomplished by using a source voltage of 70 eV, manifold temperature of 80°C and electron multiplier voltage of 1800 V. The samples were introduced by means of a Perkin Elmer Sigma 3B gas chromatograph directly interfaced to the MS. An OV-101 vitrious silica WCOT capillary column (50m x 0.2mm) was used. Masses from 40 to 300 mass units were scanned every second. Component concentrations were determined by utilizing the ion current of the enhanced spectra of each peak excluding the ion current of interfering mass ions.

Due to the time consuming analysis times involved, determination of aromatics by GC-MS was carried out for three samples only (ST-6, ST-7 and ST-14). Weight % aromatics in the other samples were calculated from NMR data (obtained with the same instrumentation as previously described) using a GC-MS/NMR correlation equation developed by Glavincevsk (40). The aromatics content of all samples as determined by MS or MS/NMR and provided by the Scientific Authority are compared with the other values in Table 7. The values are plotted against SFC values in Figure 17. A linear regression of these data gave a slope of 0.9190, an intercept of 2.506 and an r^2 value of 0.8760. The only point well outside the 95% confidence dashed lines represents the sample ST-14. It is difficult to explain why the results for this sample do not agree since a well defined cut point between saturates and aromatics is observed in the SFC chromatogram in Appendix A8-21. Furthermore, the SFC and FIA results are in reasonable agreement for this sample.

It is felt that no further interpretation of this trend should be made since distinctly different methods are being compared. As stated by Petrakis et al (13), absolute comparison of group-type concentrations by chromatographic and MS analysis should not be attempted.

Costs

A. Capital Cost:

The costs of the individual components employed in the SFC set-up at the Alberta Research Council are listed in the Table 8 along with their

suppliers. In a number of instances for which the exact equipment is no longer available, alternates and their costs are listed. The estimated equipment cost (including the refrigerated circulator bath) is $25,000. Alternatively using the prepressurized cylinder of CO_2 the cost is $22,000. This does not include assembly of the equipment.

Four commercial SFC units have recently become available. They are listed below. All units are equipped for pressure control, but integrators are not included. Prices which were quoted in US dollars have been converted to Canadian dollars using the factor 1.40.

i)Model 501	Lee Scientific 4426 So. Century Drive Salt Lake City	$74,000.00
ii)Model SFC/200A	Suprex Corporation SFC Research Center 125 William Pitt Way Pittsburgh, PA 15238	$48,000.00
iii) System Two	Brownlee Labs 2045 Martin Avenue Santa Clara, CA 95050	$63,000.00
iv) CCS 5000	Computer Chemical Systems 7000 Limestone Rd. Oxford, PA 19363	$52,000.00

The Lee and Brownlee systems include a personal computer which probably accounts for their higher costs. All of these commercial systems are designed for use with capillary columns, but should be adaptable to packed column work.

B. Cost of Analysis:
Routinely 30 injections per day can be carried out. Over a 40 day period the following materials were used:

Carbon dioxide	23.00/cylinder	(1)	23.00
Compressed Air	14.00/cylinder	(3)	42.00
Prepurified Hydrogen	26.00/cylinder	(1)	26.00
Helium	49.00/cylinder	(4)	196.00
Carbon disulfide	50.00/500 mL	(8)	400.00
Total cost of gases and solvents:			$687.00

Replacement costs for the following items (estimated number required per year in parentheses):

Column (2)	800.00
Seals for syringe pump (2)	104.00
Outlet stator for Rheodyne 7520 valve (1)	172.00
Total estimated replacement costs:	$1076.00

Assuming 240 working days per year, and the above costs as typical of materials and replacements, the cost per injection (not including operator wages) would be:

$$687/(30x40) + 1076/(30x240) = \$0.72$$

Suitability of the SFC/FID Method for Refinery Use

Since the FIA is the standard method used for aromatics analysis in refinery control laboratories, this discussion will focus upon a comparison of SFC/FID against FIA. There is no doubt that the FIA method employs simple inexpensive equipment, and that operators are easily trained. The equipment required in the SFC method is more expensive, but considerably cheaper and less elaborate than other instrumentation such as NMR or GC-MS. The SFC instrumentation has proved to be reliable since it was set up and used extensively in our laboratory for about one year. Personnel are easily trained on SFC equipment as indicated by our observation of three days for a technologist with one year of chemical laboratory experience.

Advantages of SFC over FIA include shorter analysis time, no dependence on sample color and less restrictive in terms of sample boiling range. The average analysis time by SFC is 15 min. most of which is the column elution time. The only preparation time is dilution of the sample. The FIA analysis time is of the order of two hours which includes column repacking and elution time. Highly colored samples often make analysis by FIA impossible. This is not a problem in SFC. Theoretically FIA is limited to samples with final boiling points less than 315°C, whereas samples is this study with 90% off by 385°C were analyzed by SFC and gave results which agreed with those obtained by GC-MS/NMR.

The repeatabilities of SFC and FIA were similar, about 1 wt% (or vol%) over the range of aromatics values of 20 to 80 wt% (or vol%). Absolute accuracy is difficult to determine. Analysis of the same samples by both methods did show a strong correlation (coefficient of 0.9018). Highest discrepancies occurred with high boiling samples and those with high olefins content. Olefins are included with the saturates by the SFC method described in the present work. A separate olefins determination was not part of the objectives of this work.

It is concluded that, despite the higher equipment cost, the SFC method possesses advantages over FIA for use in refinery control laboratories.

RESULTS AND DISCUSSION - AROMATICS BY RING NUMBER

Determination of Aromatics Cut Points

As stated previously, model compounds and their capacity factors for a number of conditions and stationary phases are given in Table 1B. The compounds are classified according to saturates and number of aromatic rings. Fluorene was considered a triaromatic even though it has a five-membered ring which is partially saturated. A few sulfur containing compounds were also included in this list. The criteria for good separation of component types is a small difference between k values of compounds of the same type and minimum overlap of k values for different component types. As already stated the best saturates-monoaromatics separation with our system is obtained with the 5μ silica column at 35°C and 3600 psi. The data for the silica column at both 90 and 35°C shown in Table 1B in general indicate a grouping of the aromatics according to number of rings. The only significant overlap occurs between the monoaromatic compounds, hexamethylbenzene and octahydroanthracene, and the diaromatic compounds. It is suspected that these monoaromatics overlap because of the large amount of pi electron delocalization over the ring structures. For the model compounds considered in the present work good separation is obtained between the diaromatics and polyaromatics.

As mentioned previously, the separation of polycyclic aromatic hydrocarbons by HPLC using a chemically bonded aminosilane stationary phase has been reported by Grizzle and Sablotny (19) based on the work of Wise et al (18). Alfredson (17) used a cyanopropyl column coupled to silica gel to separate saturates, olefins, aromatics and polars by HPLC. Campbell and Lee (29) have also described a semi-preparative SFC method for carrying this out using an amino-modified silica column. Capacity factor data from our system using both an NH_2 column and a series combination of Si/CN at 35°C and 3600 psi (24,800 kPa), are shown in Table 1B. The separation between mono- and diaromatics is marginally better using the Si/CN combination compared to the silica; however, as mentioned previously the saturates-monoaromatics separation is not as good. The mono- and diaromatics separation with the NH_2 column is the best comparing the three stationary phases. In this case, however, the saturates-monoaromatics separation is very poor (the k value for C_{30} is greater than most of the monoaromatics). Considering the limited number of compounds studied using the series combination of Si/Ag, it can be seen from Table 1B that this system is no better than the silica column at 90°C.

The effect of stationary phase on the separation of aromatics types is also illustrated in Figure 6 for sample ST-11. It can be seen that while the Si/CN and NH_2 provide better separation between aromatics types, neither satisfactorily separate the saturates from the monoaromatics. It is concluded that, of the stationary phases studied, silica would still be the one preferred for quantitation of aromatics according to number of rings.

For the 22 samples considered in this study the assignment of component types may be made on the basis of the chromatograms obtained at 35°C and 3600 psi shown in Appendix 7 and retention time data for model compounds given in Table 1A. The component types fall into the following approximate retention time

ranges: saturates, 3.6 to 4.1 min., monoaromatics, 4.2 to 5.0 min., diaromatics, 4.9 to 6.7 min., and polyaromatics, > 6.0 min. Ranges are given rather than distinct cut points because of the lack of pressure control in our system. Unfortunately, this lack of pressure control which has already been mentioned is a limitation in carrying out quantitation of aromatics according to the number of rings.

Calibration of Aromatic Types

Sample ST-11 was chosen for separation by column chromatography since, of all the samples studied, it contained the largest of each aromatic fraction. Two batches of sample of about 1g each were separated on the silica-alumina column in order to obtain sufficient material for calibration of the aromatic types. The percentages of each fraction recovered are listed in Table 9. The recovery is close to 100% presumably because this sample is quite high boiling as seen by the simulated distillation data in Appendix 1. The SFC chromatograms of each fraction from one separation are shown in Figure 18. Each fraction appears to be reasonably pure, indicating that the SFC method provides a separation similar to that of the column chromatographic procedure. The SFC separation conditions were not optimum for these runs (90°C and 3250 psi); however, this should not affect the calibration.

The calibration curves obtained for the aromatic fractions, over a concentration range which spans that expected from actual samples, are shown in Figure 19. The data points, which are given in Table 10, were fitted to the curve $y = A * x$. The slopes, A, (or response factors) shown in Figure 19 for the mono- and diaromatics are similar, whereas that for the polyaromatics is approximately 15% lower. This lower value is suspected to be due to the presence of heteroatoms such as sulfur and tertiary aromatic carbon atoms in this fraction, both of which would be expected to decrease the FID response. It would be possible to correct for this lower response in determining the aromatic types; however, for most samples the polyaromatic concentration was very small and the effect on the overall results would be minimal. Therefore, it is suggested that the aromatic types be determined directly from the integrated peak areas with appropriate correction for the area of the CS_2 solvent impurity peak.

Comparison of SFC and GC-MS/NMR Results

At this time the separation of aromatic types using SFC is considered the best with the silica column at 35°C and 3600 psi. However, there are two problems which prevent it from being applicable to a wide variety of samples. First, the lack of pressure control results in poor retention time repeatability which makes it difficult to determine the cut points. Secondly, there is overlap between mono- and diaromatic compound types. However, it was thought useful to compare the aromatic type results which could be determined by SFC with those determined by an established method, GC-MS. Because of time limitations only three samples, ST-6, ST-7 and ST-14 were directly analyzed by GC-MS. The remainder were calculated from NMR measurements using a correlation formula developed by Glavincevsk (40), and described as GC-MS/NMR. Results are listed in Table 11. The GC-MS/NMR results were supplied by the Scientific Authority. In the case of about half the samples it was necessary to combine the mono- and diaromatics because of the overlap of the peaks in the SFC chromatograms.

The results in Table 11 do indicate a reasonable correspondence between the monoaromatics results. The diaromatics are generally lower by SFC and the polyaromatics higher by SFC. The only other method for which a comparison may be made for one of the samples is the silica-alumina column method. The data for sample ST-11 in Table 11 actually agree very well with the data in Table 9. This merely indicates that the SFC and column methods do provide a similar separation (as was shown qualitatively in Figure 18) of component types, which does not agree that well with the GC-MS/NMR method.

In order to allow separation and quantification of aromatic types for a wider range of samples than is currently possible two changes should be made. First of all, it is recommended that pressure control be installed in our SFC system which will provide better retention time repeatability. Secondly, it is suggested that better separation would result using a column switching technique. The saturates would first be separated from the aromatics on a silica column followed by separation of the aromatic types on a CN or NH_2 column with some pressure programming.

CONCLUSIONS AND RECOMMENDATIONS

A method employing supercritical fluid chromatography with flame ionization detection, similar to that reported by Norris and Rawdon (5), has been developed for the analysis of middle distillates and diesel fuels. This method generally meets the objectives as originally set out, namely one with superior or at least equivalent accuracy, precision and analysis time to FIA, and to be suitable for refinery control laboratories. Repeatabilities of the SFC and FIA methods are about the same, 1 wt% in the 20 to 80 wt% aromatics range. Absolute accuracy is difficult to measure, but the results from samples analyzed by both methods were strongly correlated. Other advantages of SFC over FIA include a shorter analysis time, no limitation according to sample color and less restricted by sample boiling range. Although SFC equipment is more costly, it is still fairly simple and operators are easily trained. Therefore, it is concluded that the SFC method is suitable for use in refinery control laboratories.

The SFC method does have some potential limitations. Samples must be diluted in CS_2 because of the non-linearity of saturates at high concentration. Detector "spiking" was observed for samples with 90% distilled at 370°C or higher when the restrictor was not placed high enough in the FID, but proper placement appeared to eliminate this problem. The calculation of sample recoveries is unreliable, which could be the result of poor repeatability of the injector. This has no effect on the aromatics determination which depends on relative area measurements. It is recommended that a study be carried out on the use of an internal standard in order to determine sample recoveries.

Comparisons were also carried out between SFC results and those obtained by NMR and by GC-MS using a correlation between GC-MS and NMR. There is a fairly strong correlation between SFC and NMR results. The data indicate that an average of 70% of the carbon atoms in the aromatic molecules of the samples studied are contained in aromatic rings, the remainder in alkyl side chains. There was also a good correlation between SFC and GC-MS/NMR.

The capital cost of equipment required to set up an SFC/FID system similar to the one at Alberta Research Council is estimated at $22,000. The cost per injection, taking into account average usage of consumables and replacement parts, and assuming 30 injections per day and 240 working days per year worked out to be $0.72.

The potential exists for determination by SFC/FID of aromatics according to the number of rings. Using the system described in the present work there is too much overlap between aromatic types to provide good quantitative data. It is recommended that two changes in the system be investigated to solve this problem. First, a facility for pressure control should be installed which will provide good retention time repeatability. Secondly, a system for column switching should be implemented which would allow for saturates separation from monoaromatics with a silica column followed by separation of the aromatics according to the number of rings by means of a cyano or amino column with the use of pressure programming.

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TABLE 1A

Retention Times of Some Model Compounds Using Different Stationary Phases*

Compound	Silica 90°C	Silica 35°C	Si/CN 35°C	NH_2 35°C	Si/Ag 35°C
Saturates:					
CS_2	4.98	3.30	6.84	4.45	5.16
N-pentane	-	-	-	-	5.16
N-hexane	4.98	-	-	-	-
3-Methylheptane	5.09	-	-	-	-
N-decane	5.16	3.30	-	-	-
Cyclohexane	5.19	-	-	-	-
Dimethylcyclohexane	5.21	3.43	-	4.45	-
Hexadecane	5.54	-	-	-	-
Decalin	5.61	3.48	-	-	-
Eicosane (C_{20})	5.86	3.42	-	-	6.03
Triacontane (C_{30})	-	3.59	7.87	9.42	6.50
Monoaromatics:					
Benzene	5.76	3.85	-	-	-
Toluene	5.92	3.85	-	-	-
3-Ethyltoluene	6.20	3.84	-	-	-
O-xylene	6.27	3.95	7.87	5.66	6.50
Indane	6.22	4.11	-	-	-
1-Phenydecane	6.94	4.09	-	-	-
Tetralin	7.01	-	8.67	7.20	-
Hexamethylbenzene	8.41	-	10.08	9.42	-
Octahydroanthracene	8.96	-	10.50	11.69	-
Diaromatics:					
Naphthalene	7.60	4.53	9.65	9.42	7.70
2-Methylnaphthalene	7.78	-	10.08	10.12	-
Thianaphthalene	7.78	-	10.08	10.12	-
Biphenyl	8.48	-	9.88	10.95	-
Acenaphthalene	8.96	-	11.26	-	-
Bibenzyl	9.57	-	10.71	-	-
Polyaromatics:					
Fluorene	10.08	-	-	-	-
Dibenzothiophene	10.74	-	-	-	-
Anthracene	11.06	-	-	-	-
Phenanthrene	11.28	6.11	14.74	26.04	10.72
Thianthrene	13.72	-	-	-	-
Fluoranthene	14.06	-	19.00	-	-
Pyrene	14.54	-	-	-	-
Chrysene	-	9.53	-	-	-

* All runs were carried out at a pressure of 3600 psi.

Blank (-) data indicate that the given compound was not run under the stated conditions.

TABLE 1B

Comparison of Capacity Factors of Some Model Compounds Using Different Stationary Phases*

Compound	Silica 90°C	Silica 35°C	Si/CN 35°C	NH_2 35°C	Si/Ag 35°C
Saturates:					
N-pentane	-	-	-	-	0.00
N-hexane	0.00	-	-	-	-
3-Methylheptane	0.02	-	-	-	-
N-decane	0.04	0.00	-	-	-
Cyclohexane	0.04	-	-	-	-
Dimethylcyclohexane	0.05	0.04	-	0.00	-
Hexadecane	0.11	-	-	-	-
Decalin	0.13	0.05	-	-	-
Eicosane (C_{20})	0.18	0.04	-	-	0.17
Triacontane (C_{30})	-	0.09	0.15	1.12	0.26
Monoaromatics:					
Benzene	0.16	0.17	-	-	-
Toluene	0.19	0.17	-	-	-
3-Ethyltoluene	0.24	0.16	-	-	-
O-xylene	0.26	0.20	0.15	0.27	0.26
Indane	0.33	0.25	-	-	-
1-Phenydecane	0.39	0.24	-	-	-
Tetralin	0.41	-	0.27	0.62	-
Hexamethylbenzene	0.69	-	0.47	1.12	-
Octahydroanthracene	0.80	-	0.54	1.62	-
Diaromatics:					
Naphthalene	0.53	0.37	0.41	1.12	0.49
2-Methylnaphthalene	0.56	-	0.47	1.27	-
Thianaphthalene	0.56	-	0.47	1.27	-
Biphenyl	0.70	-	0.44	1.46	-
Acenaphthalene	0.80	-	0.65	-	-
Bibenzyl	0.92	-	0.57	-	-
Polyaromatics:					
Fluorene	1.02	-	-	-	-
Dibenzothiophene	1.16	-	-	-	-
Anthracene	1.22	-	-	-	-
Phenanthrene	1.27	0.85	1.15	4.85	1.08
Thianthrene	1.76	-	-	-	-
Fluoranthene	1.82	-	1.78	-	-
Pyrene	1.92	-	-	-	-
Chrysene	-	1.89	-	-	-

* All runs were carried out at a pressure of 3600 psi.

TABLE 2

Percentages of Saturates and Aromatics Recovered by Column Chromatography* from Several Samples

Sample	Wt% Saturates	Wt% Aromatics	% Recovery
HAD	25.5	73.5	99.0
3256	44.6	45.5	90.1
102	73.7	22.7	96.4
284	75.2	6.1	81.3

* Sawatzky et al, Reference (33).

TABLE 3

Accuracy of SFC/FID Determined Using Known Mixtures of Naphthalene and Hexadecane*

Wt% Naphthalene		Difference
Actual	Found	
20.4	19.8	0.6
40.1	40.2	-0.1
48.4	48.7	-0.3
60.3	60.3	0.0
79.8	80.7	-0.9

* Conditions were 3250 psi and 90°C.

TABLE 4

Aromatics Content by SFC/FID of Multiple Analyses of Middle Distillate Samples Under Different Conditions

	90°C, 3250 psi		90°C, 3600 psi		35°C, 3600 psi	
Sample	Mean Wt%	Std Dev	Mean Wt%	Std Dev	Mean Wt%	Std Dev
8	30.2	0.6	32.3	0.9	40.3	0.0
102	29.6	0.3	28.8	0.0	30.7	0.0
103	31.4	0.8	33.5	0.6	34.6	0.7
185	35.3	0.6	38.3	1.2	37.1	0.4
187	33.8	0.1	29.4	1.5	42.9	0.1
281	30.3	0.2	30.0	0.3	39.1	0.9
284	21.7	1.2	28.7	0.6	30.4	1.0
3200	37.1	0.3	45.9	0.3	46.8	0.1
3256	47.3	2.1	52.7	0.2	55.2	0.1
3259	34.7	0.9	31.7	0.0	46.4	0.4
LAD	25.0	0.6	25.6	0.6	25.4	0.1
HAD	77.4	0.1	77.7	0.1	80.8	0.3
ST-3	37.9	0.1	32.5	0.4	23.8	0.1
ST-4	16.0	0.0	15.0	0.1	28.4	0.8
ST-6	27.9	0.8	40.5	0.1	50.2	0.1
ST-7	42.4	0.9	39.2	1.4	49.5	0.2
ST-8	45.7	0.3	42.6	0.2	51.7	0.1
ST-10	66.6	0.8	60.4	0.1	69.6	0.2
ST-11	78.1	1.3	77.0	0.5	78.0	1.2
ST-12	20.9	0.1	21.8	0.4	32.0	0.3
ST-14	24.5	0.5	32.4	0.1	37.6	0.1
ST-21	26.3	1.0	31.7	1.1	37.7	0.0
s_{pooled} (wt%)		1.0		0.9		0.4
Repeatability* (wt%)		2.8		2.6		1.1

* "Duplicate measurements by the same operator should be considered suspect if they differ by more than this amount 19 times out of 20."

TABLE 5

Sample Recoveries Calculated from SFC Data

Sample	Mean % Recovery	Std Dev
HAD	105.7	14.5
284	101.5	3.5
102	98.1	14.1
3256	93.5	12.6

TABLE 6

Comparison of SFC and FIA Data

Sample	SFC	FIA		
	Wt% Aromatics*	Vol% Aromatics	Vol% Olefins	90% off Temp (°C)
8	40.3	35.0	1.1	331
102	30.7	28.9	2.1	313
103	34.6	41.8	5.6	374
185	37.1	46.7	6.8	369
187	42.9	37.0	1.3	340
281	39.1	33.3	1.3	331
284	30.4	25.0	1.3	288
3200	46.8	39.1	1.1	319
3256	55.2	63.9	18.8	341
3259	46.4	44.7	1.7	328
LAD	25.4	19.6	1.0	254
HAD	80.8	74.2	2.5	318
ST-3	23.8	20.6	1.9	230
ST-4	28.4	24.1	1.5	300
ST-6	50.2	44.9	1.4	333
ST-7	49.5	43.7	1.6	367
ST-8	51.7	44.2	1.6	345
ST-10	69.6	64.0	2.1	379
ST-11	79.0	75.0	1.9	385
ST-12	32.0	24.9	1.6	319
ST-14	37.6	33.3	1.8	326
ST-21	37.7	33.0	2.2	326

Linear regression data — SFC vs FIA

slope:	0.9734±0.0718
intercept:	-2.199±3.356
r^2:	0.9018

* 35°C, 3600 psi

TABLE 7

Comparison of Aromatics Data by SFC, NMR and GC-MS/NMR

Sample	SFC Wt% Aromatics[1]	NMR % Aromatic Carbon	GC-MS/NMR Wt% Aromatics
8	40.3	28.8	42.6
102	30.7	19.1	30.4
103	34.6	20.9	29.9
185	37.1	24.1	38.5
187	42.9	29.8	41.9
281	39.1	27.2	39.6
284	30.4	21.4	35.0
3200	46.8	33.5	47.2
3256	55.2	35.1	59.0
3259	46.4	26.2	40.8
LAD	25.4	19.6	29.4
HAD	80.8	59.9	85.2
ST-3	23.8	22.4	26.3
ST-4	28.4	18.6	28.0
ST-6	50.2	25.1	45.6[2]
ST-7	49.5	33.1	46.4[2]
ST-8	51.7	33.7	47.1
ST-10	69.6	47.2	62.3
ST-11	79.0	51.9	73.9
ST-12	32.0	19.3	30.9
ST-14	37.6	14.7	20.4[2]
ST-21	37.7		

Linear regression data	SFC vs NMR	SFC vs GC-MS/NMR
slope:	0.6866±0.0547	0.9190±0.0793
intercept:	-1.395±2.579	2.506±3.738
r^2:	0.8923	0.8760

[1] 35°C, 3600 psi
[2] Actually determined by GC-MS

TABLE 8

Equipment Costs of the SFC/FID System at Alberta Research Council

ARC Equipment	Alternate Equipment	Approx. Cost $
A. Refrigerated circulator bath Lauda Model 4KR (no longer available)	Lauda Model RCS-6 or equivalent Brinkmann Instruments 50 Galaxy Blvd. Rexdale, Ontario	(3000.00)
B. Syringe Pump Varian 8500 (no longer available)	ISCO model LC-2600 Technical Marketing Assoc. 1661 Finfar Court Mississauga, Ontario	8000.00
C. SSI valves 3-way valves 1-way valve Mandel Scientific 143 Dennis St. Rockwood, Ontario		 200.00 200.00
D. Sampling Valve Rheodyne model 7520 with 0.2μL internal sample loop Sulpelco Inc. 46-220 Wyecroft Road Oakville, Ontario		600.00
E. Pressure Gauge Marsh Model D3990BZ Fleck Bros Edmonton	Alltech flow through gauge 0-6000 psig Model 9299 Mandel Scientific	270.00
F. Chromatographic columns Alltech 5μ silica 2.1 mm ID X 250 mm length Mandel Scientific Cat no. A-9963		 400.00
G. Gas Chromatograph Shimadzu Model GC-8A Tekscience 1100 Invicta Drive Oakville, Ontario		 8000.00

TABLE 8 (cont'd)

H.Restrictors		
10μ flexible fused uncoated silica capillary tubing		250.00 for 40
Spectran Corporation Hall Road,P.O. Box 650 Sturbridge, Mass.		
or	Polymicro Technologies 3035 N 33rd Drive Phoenix,AZ 85017	120.00 for 40 meters
I.Graphite ferrules		
40 % graphatized vespel Supelco Inc Cat. no. C13260		47.00 pkg of 10
or	Cat. no. 2-2480 Chromatographic Specialties P.O.Bag 1150 300 Laurier Blvd. Brockville, Ontario	42.00 pkg of 10
J.Integrator Spectra Physics Model 4290 Technical Marketing Assoc.		3000.00
K.Miscellaneous		
1,2,5,10 mL volumetric flasks Fisher Scientific		150.00 per dozen
100 and 250μL gas tight syringes Chromatographic Specialties		60.00 ea
1.59 mm (1/16") OD X 0.1 mm ID (.004") S.S. tubing Mandel Scientific Cat no. 30213		25.30 per meter
Gas Regulators and Inline filter Inline filter holder 450 Inline filter 452 Matheson Gas Products		250.00ea 100.00 50.00

Total cost: (including circulator bath) approximately ($25,000.00)

(without bath, if prepressurized CO_2 used) 22,000.00

TABLE 9

Percentages of Saturates and Aromatic Types Recovered by Column Chromatography* for Sample ST-11

	Wt %
Saturates	24.5
Monoaromatics	19.6
Diaromatics	34.0
Polyaromatics	21.4
Recovery:	99.5

* Sawatzky et al, Reference (33).

TABLE 10

Calibration Data for Mono-, Di- and Polyaromatics

Aromatic Type	Concentration (μg/μL)	Area Counts (x10,000)
Monoaromatic	1.91	125
	3.81	170
	7.61	282
	15.21	1013
	26.80	1895
	30.41	2069
	40.19	2701
	53.59	3784
	66.99	4375
	67.57	4559
	80.39	5462
	93.79	5503
Diaromatic	2.83	220
	7.07	509
	11.05	731
	17.67	1193
	22.09	1545
	56.45	3730
	84.67	5903
Polyaromatic	13.99	653
	27.98	1567
	41.98	2021
	55.97	3172
	69.96	4414
	83.95	5252
	97.94	5373
	111.94	6013

TABLE 11

Comparison of Aromatic Types by SFC* and GC-MS/NMR

Sample	Monoaromatics		Diaromatics		Polyaromatics	
	SFC	GC-MS/NMR	SFC	GC-MS/NMR	SFC	GC-MS/NMR
8	16.9	12.8	18.4	27.4	4.3	1.3
102	Mono + Di		28.8	27.8	1.1	1.3
103	Mono + Di		33.7	29.8	0.5	1.4
185	Mono + Di		28.8	34.2	8.5	1.3
187	17.3	14.1	21.5	27.8	2.8	<1
281	14.9	12.0	19.8	26.1	3.4	<1
284	Mono + Di		28.8	32.1	1.0	<1
3200	19.3	13.5	20.5	33.0	6.0	<1
3256	Mono + Di		47.9	57.5	6.0	1.2
3259	Mono + Di		43.8	39.9	1.4	2.5
LAD	Mono + Di		23.9	29.4	--	<1
HAD	12.7	13.7	58.7	73.5	7.9	2.1
ST-3	22.7	25.2	--	--	--	<1
ST-4	Mono + Di		26.8	27.8	0.3	<1
ST-6	22.1	22.1	20.7	17.3	6.0	2.2
ST-7	21.3	29.4	17.7	14.3	9.5	1.5
ST-8	20.1	N/D	20.5	N/D	9.0	N/D
ST-10	20.3	19.7	28.6	44.7	19.3	1.5
ST-11	21.0	23.9	36.3	49.8	18.3	<1
ST-12	Mono + Di		29.2	30.4	1.5	<1
ST-14	Mono + Di		34.8	19.7	2.0	<1
ST-21	Mono + Di		34.9	19.7	1.7	<1

* Silica column, 35°C, 3600 psi.

Figure 1A : Schematic of SFC / FID

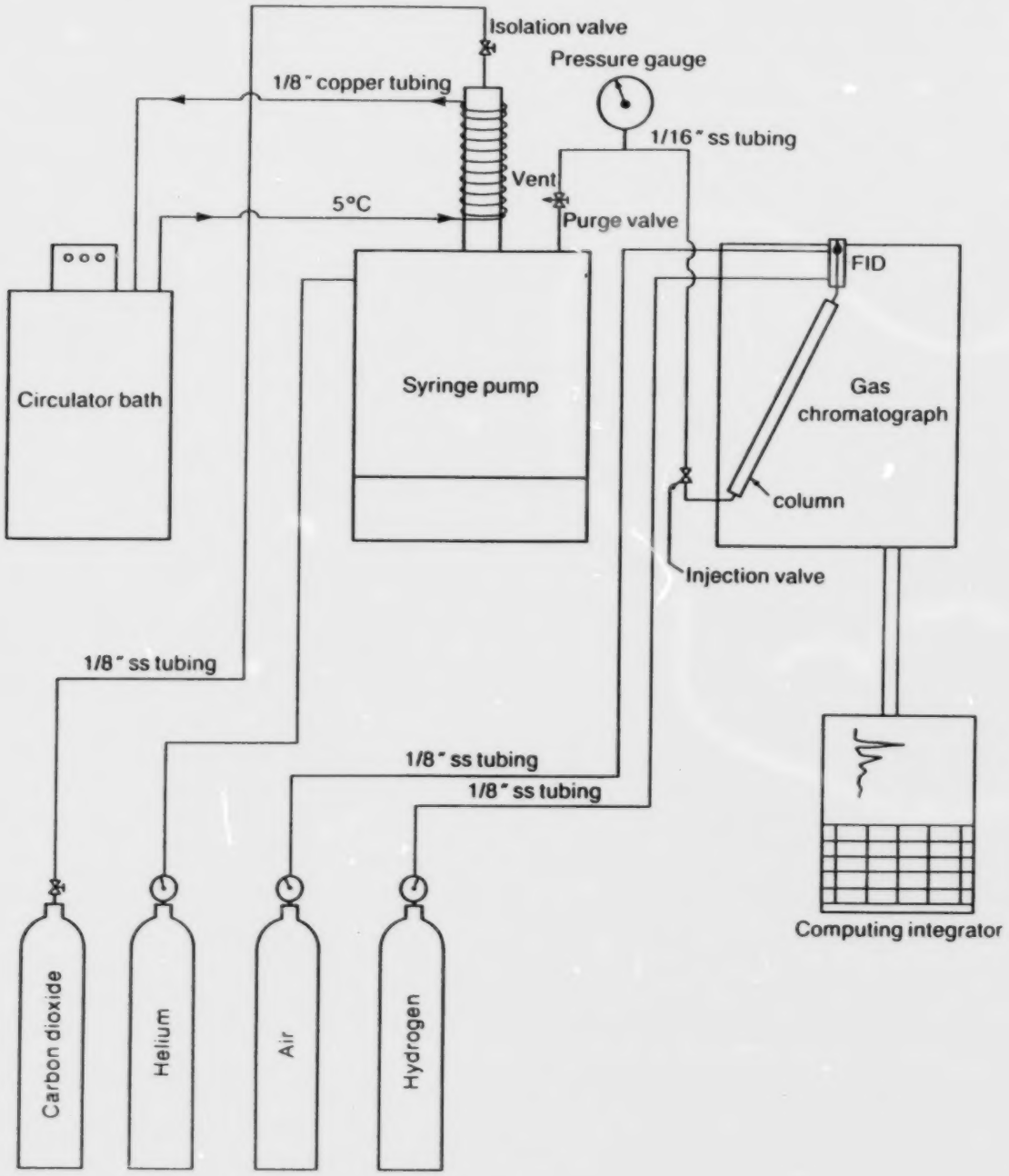


Figure 1B : Photograph of the SFC/FID system
at the Alberta Research Council.

Figure 2: Schematic of flame ionization detector, showing restrictor.

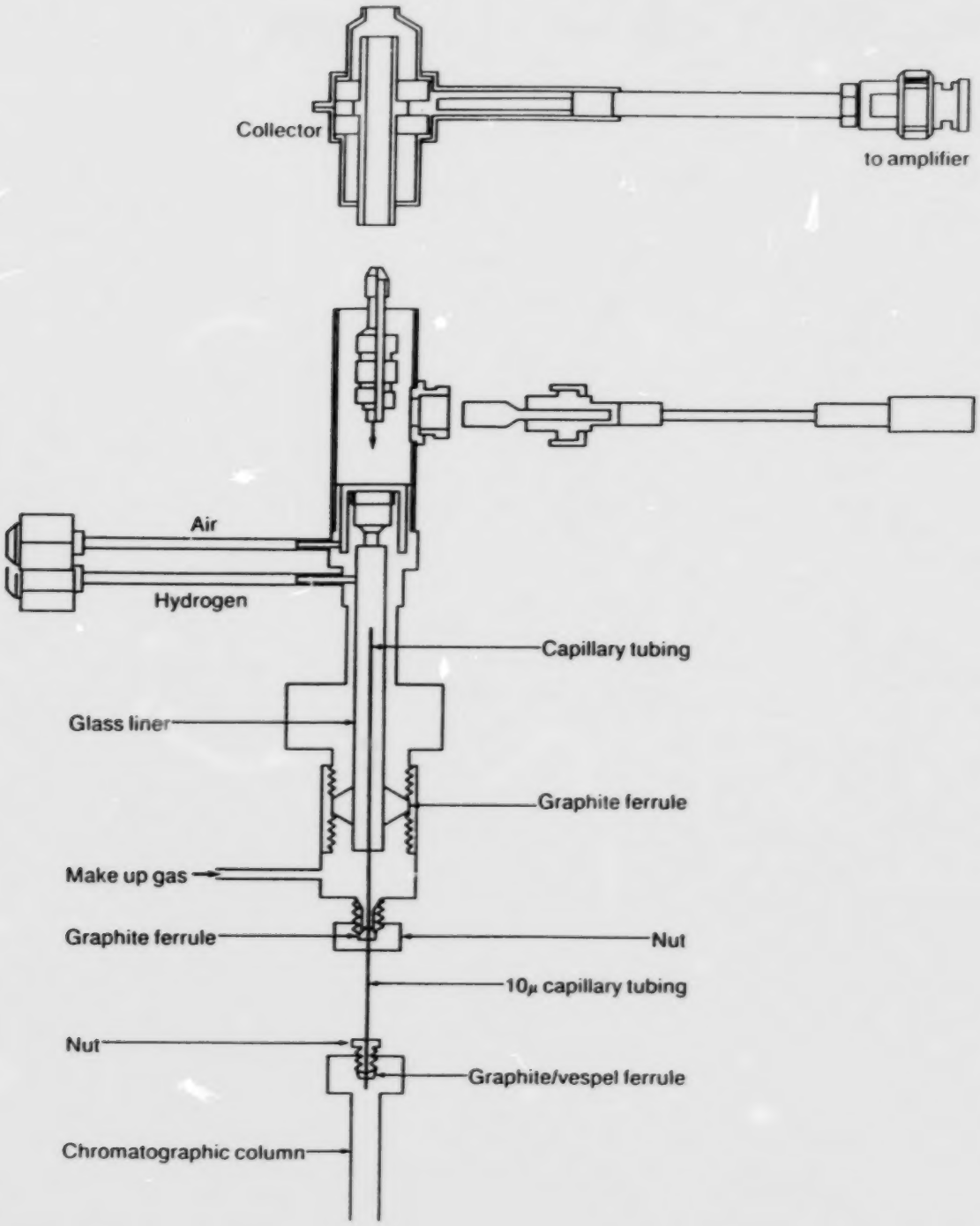


Figure 3: Summary of operating procedure for determination of aromatics by SFC

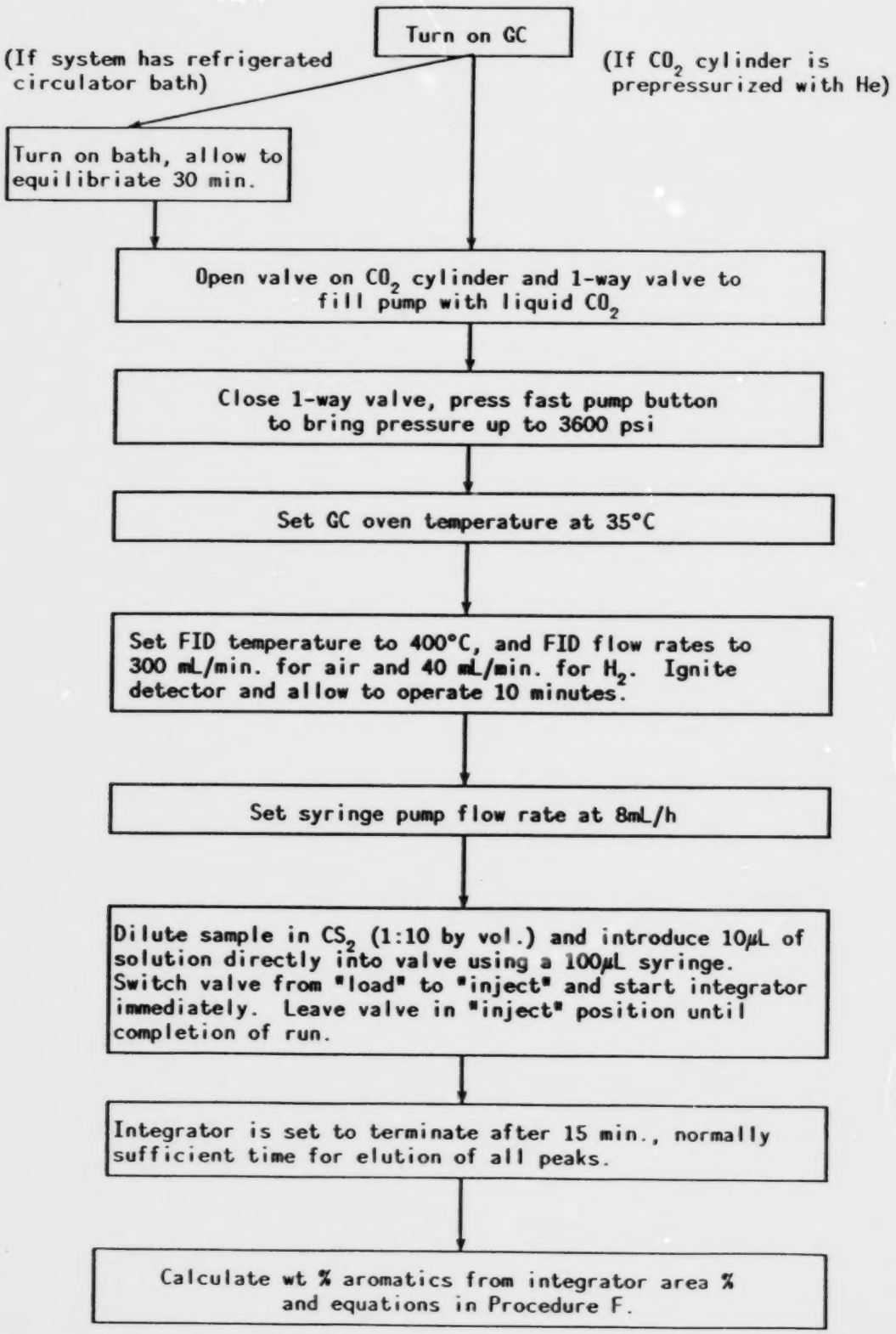

Turn on GC
(If system has refrigerated circulator bath)
(If CO_2 cylinder is prepressurized with He)
Turn on bath, allow to equilibriate 30 min.
Open valve on CO_2 cylinder and 1-way valve to fill pump with liquid CO_2
Close 1-way valve, press fast pump button to bring pressure up to 3600 psi
Set GC oven temperature at 35°C
Set FID temperature to 400°C, and FID flow rates to 300 mL/min. for air and 40 mL/min. for H_2. Ignite detector and allow to operate 10 minutes.
Set syringe pump flow rate at 8mL/h
Dilute sample in CS_2 (1:10 by vol.) and introduce 10μL of solution directly into valve using a 100μL syringe. Switch valve from "load" to "inject" and start integrator immediately. Leave valve in "inject" position until completion of run.
Integrator is set to terminate after 15 min., normally sufficient time for elution of all peaks.
Calculate wt % aromatics from integrator area % and equations in Procedure F.

Figure 4 : SFC chromatograms of a sample at temperatures of 90 and 35°C using a silica column and pressure of 3600 psi.

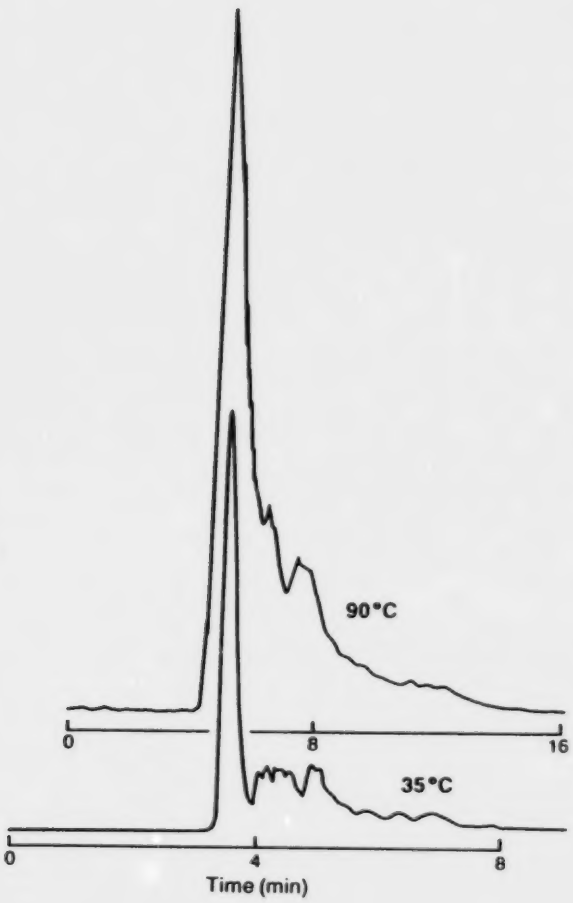


Figure 5 : Effect of pressure on the SFC chromatogram of ST-11 at 90°C.

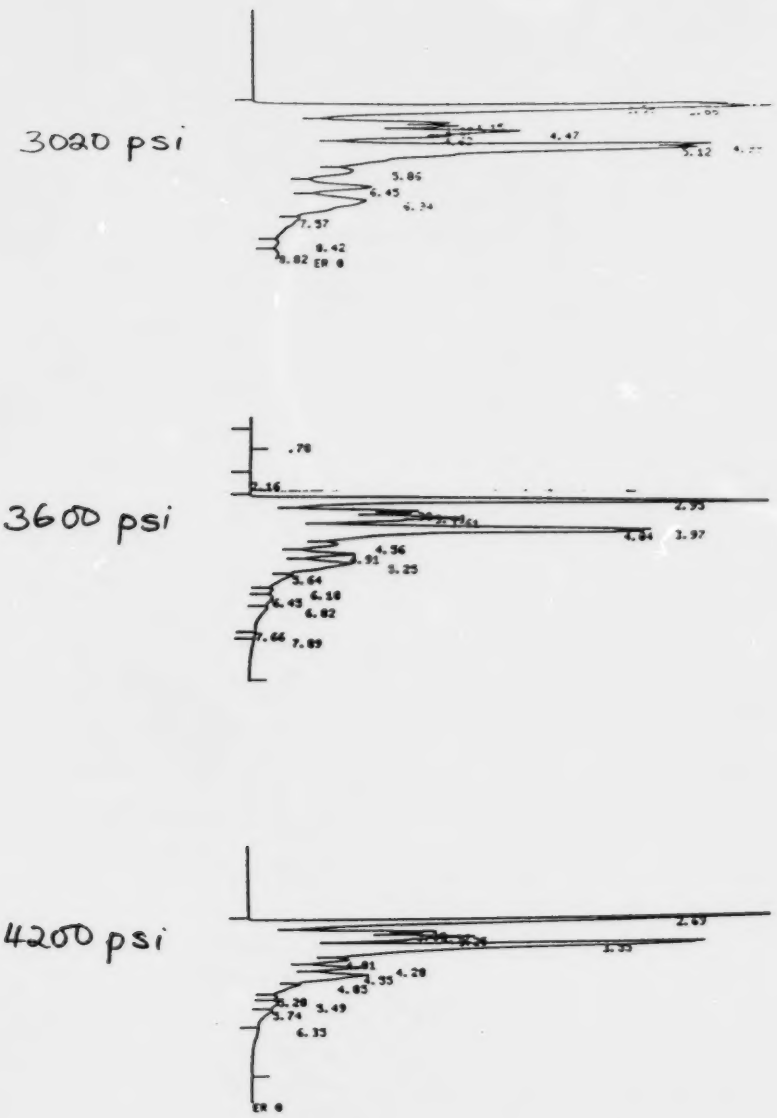


Figure 6 : Effect of stationary phase on saturates-aromatics separation by SFC at 35°C and 3600 psi for sample ST-11.

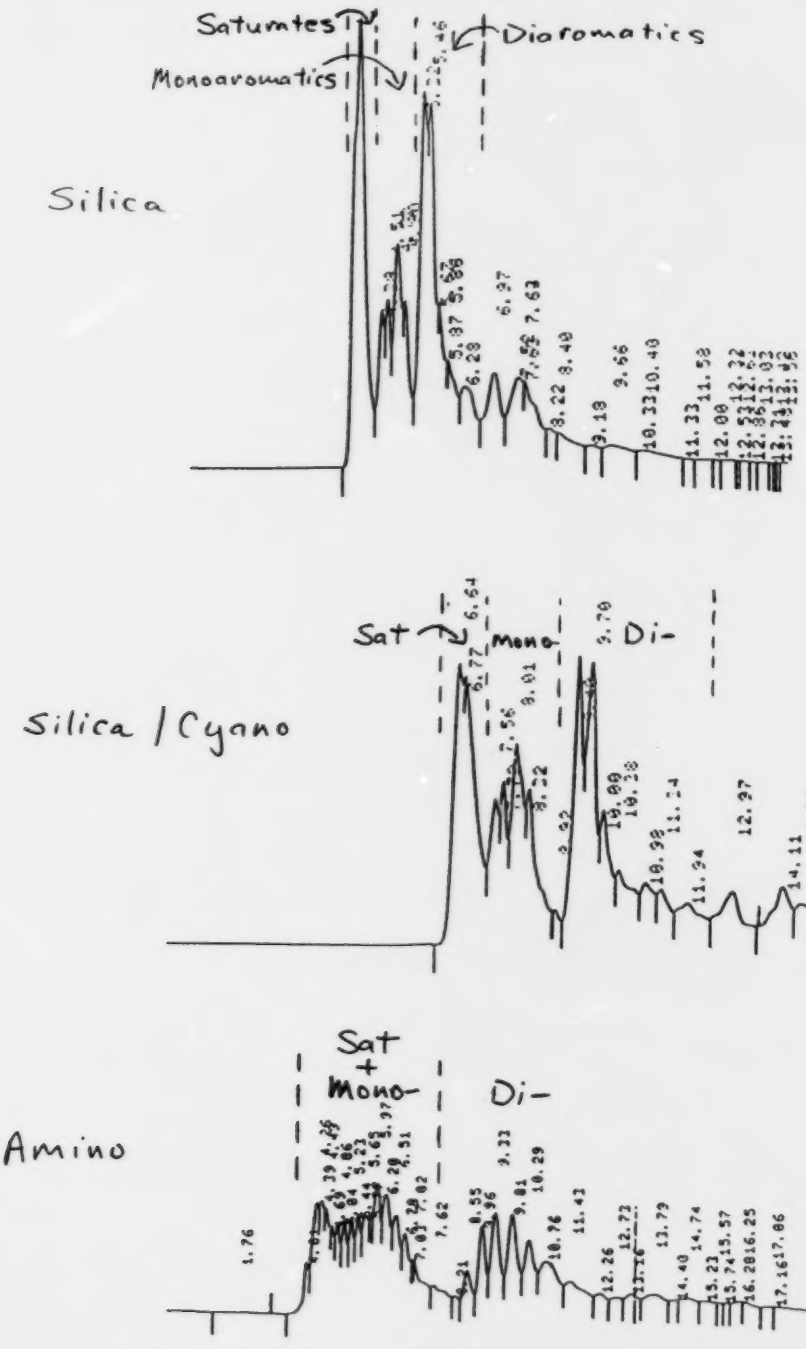
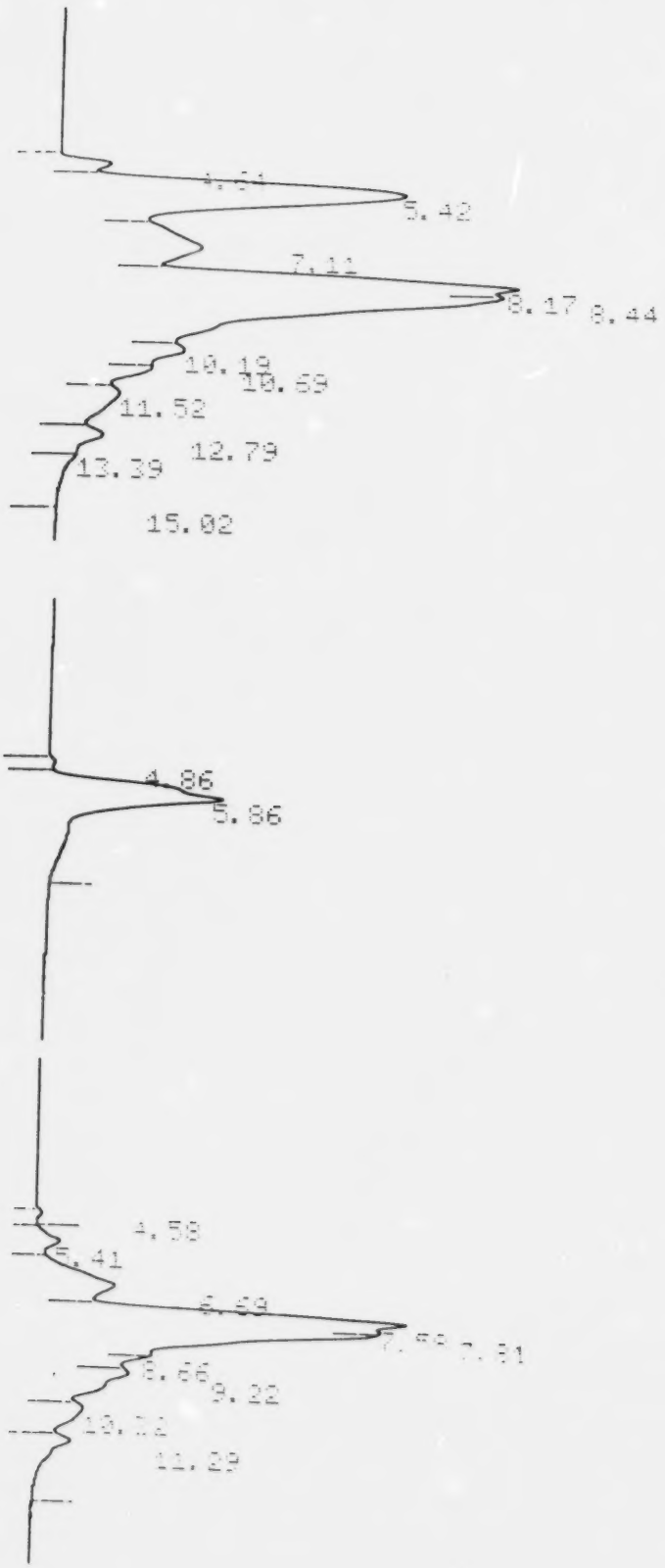


Figure 7 : SFC chromatograms of sample HAD and of its saturates and aromatics fractions after separation by column chromatography.

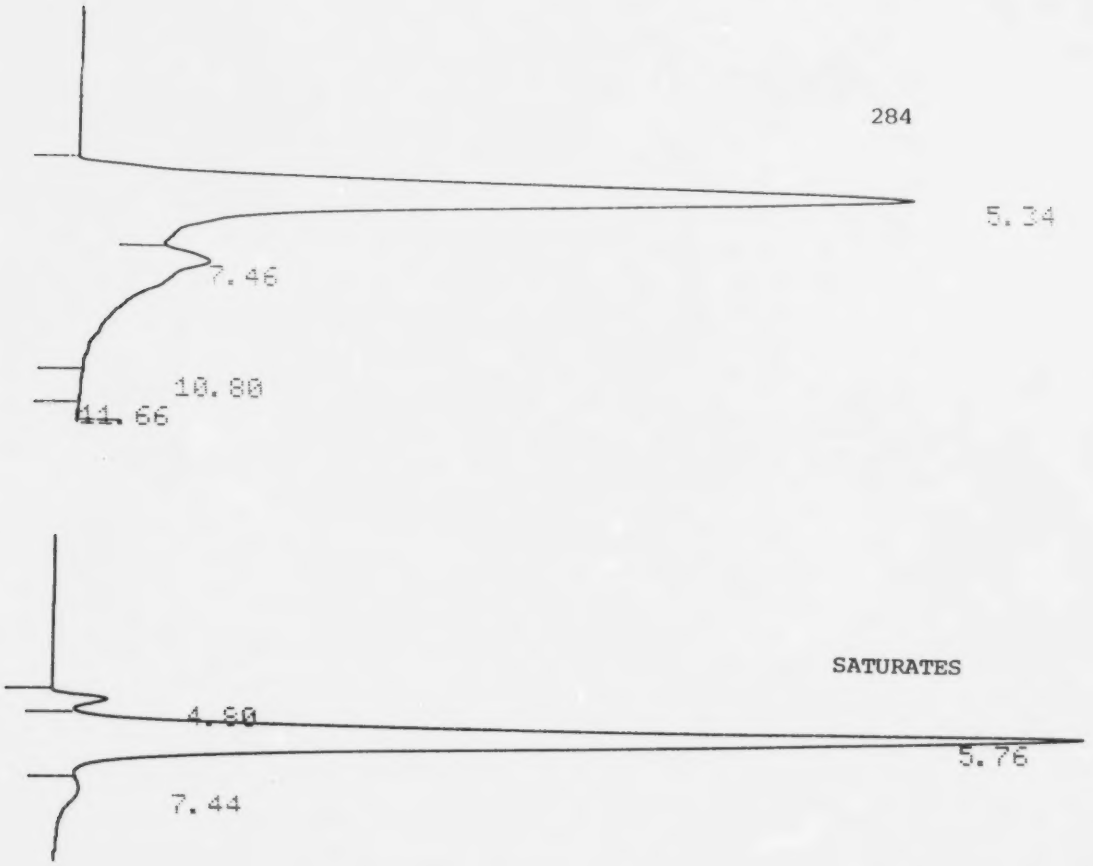


HAD

SATURATES

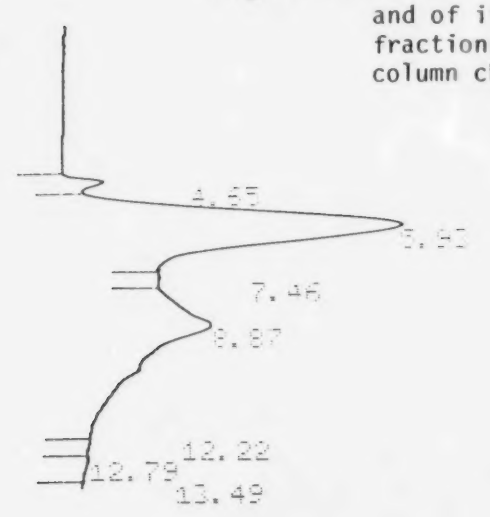
AROMATICS

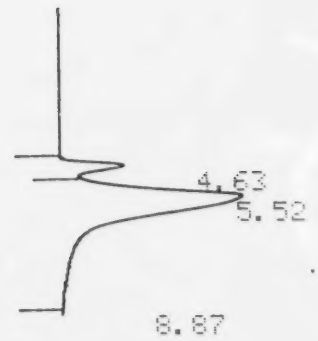
Figure 8 : SFC chromatograms of sample 284 and of its saturates fraction after separation by column chromatography.



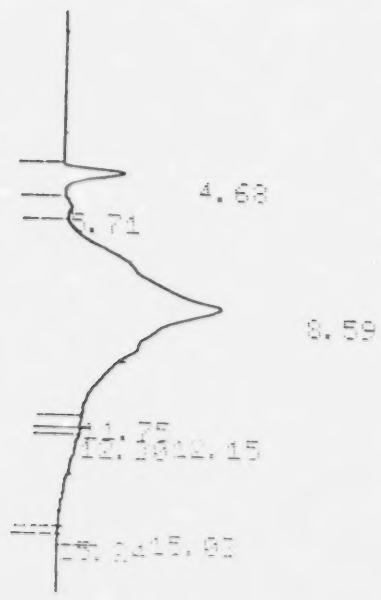
Insufficient aromatics fraction.

Figure 9 : SFC chromatograms of sample 3256 and of its saturates and aromatics fractions after separation by column chromatography.





SATURATES



AROMATICS

Figure 10 : SFC chromatograms of sample 102 and of its saturates and aromatics fractions after separation by column chromatography.

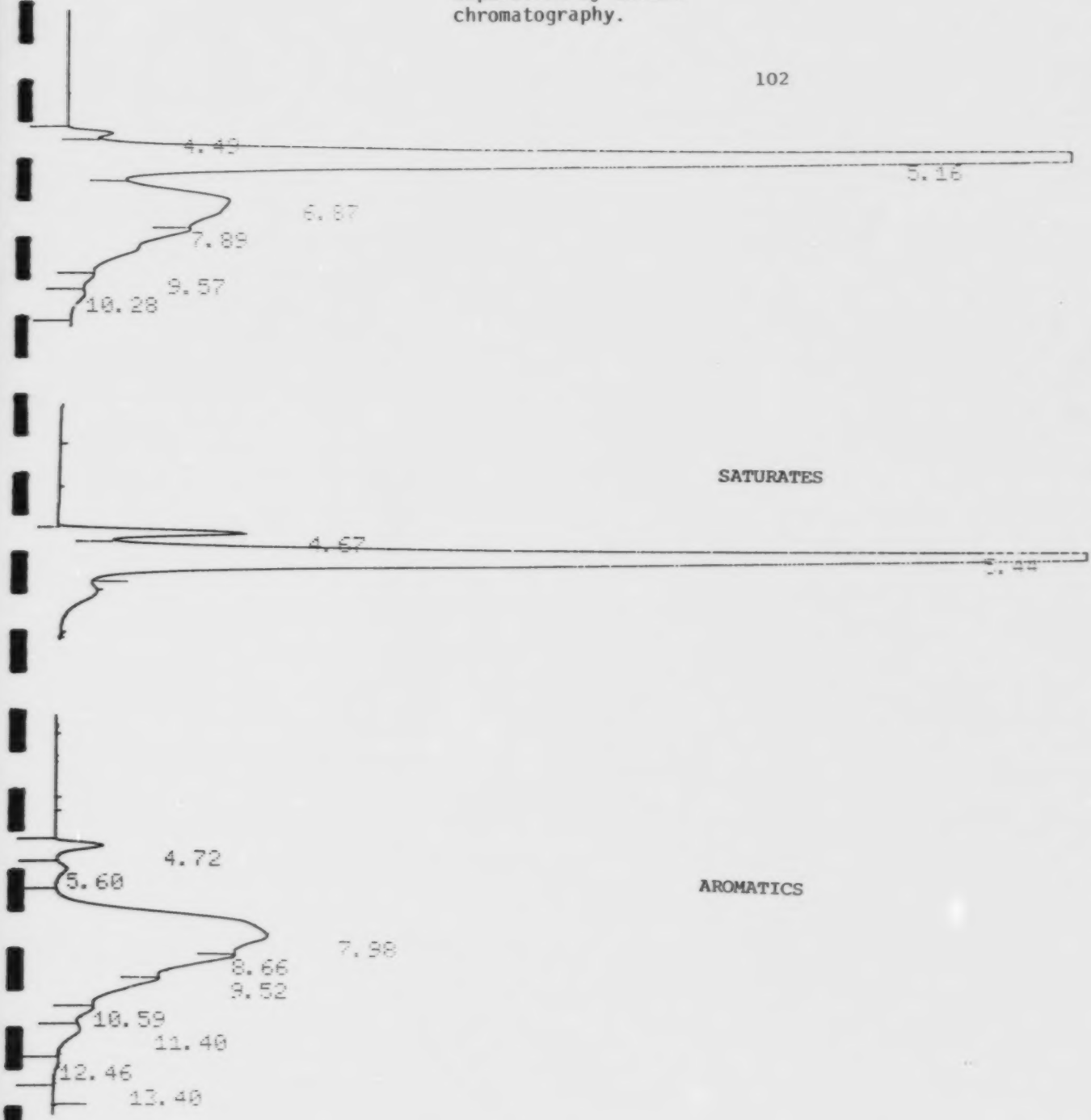


Figure 11: Saturates and aromatics calibration

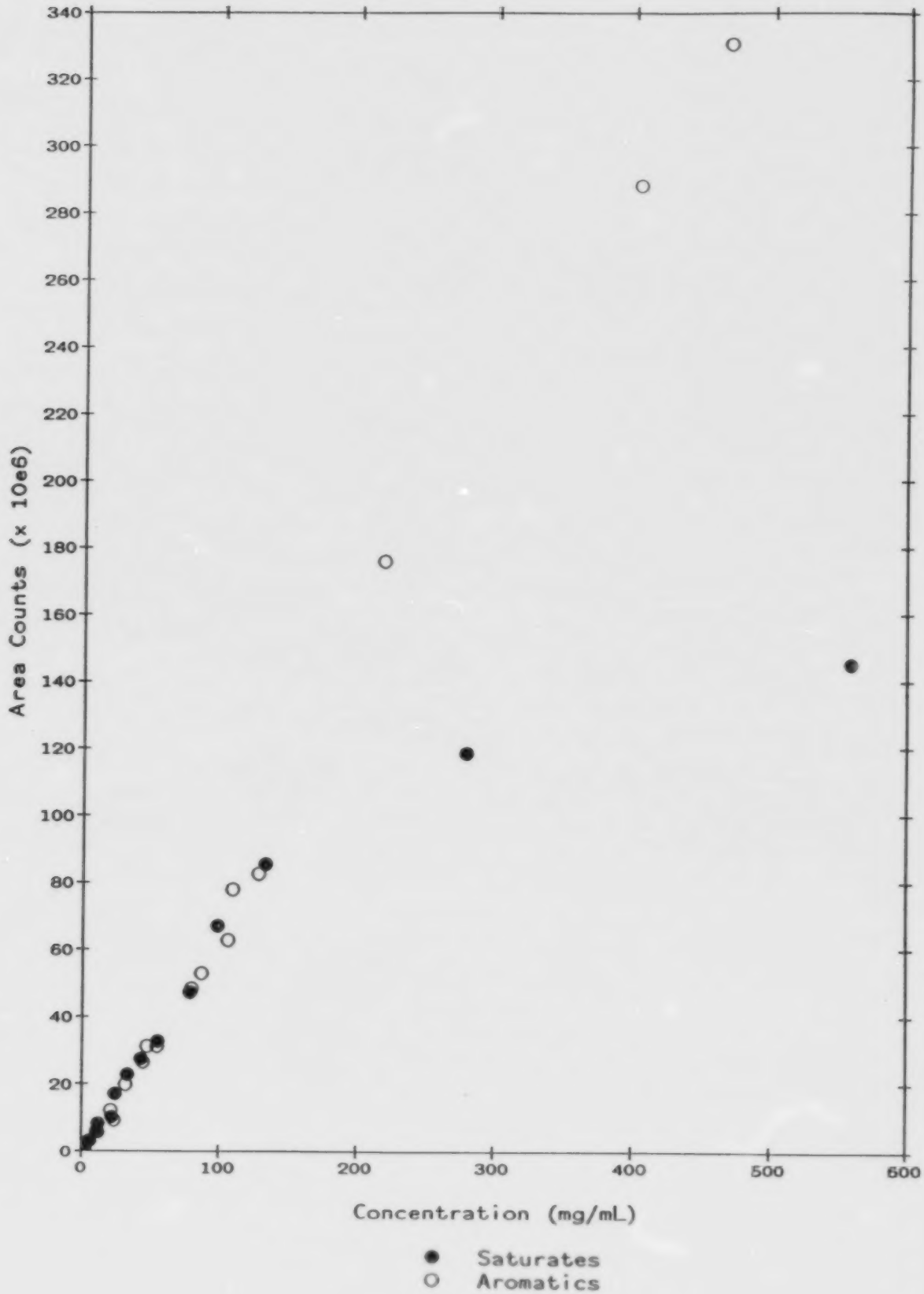
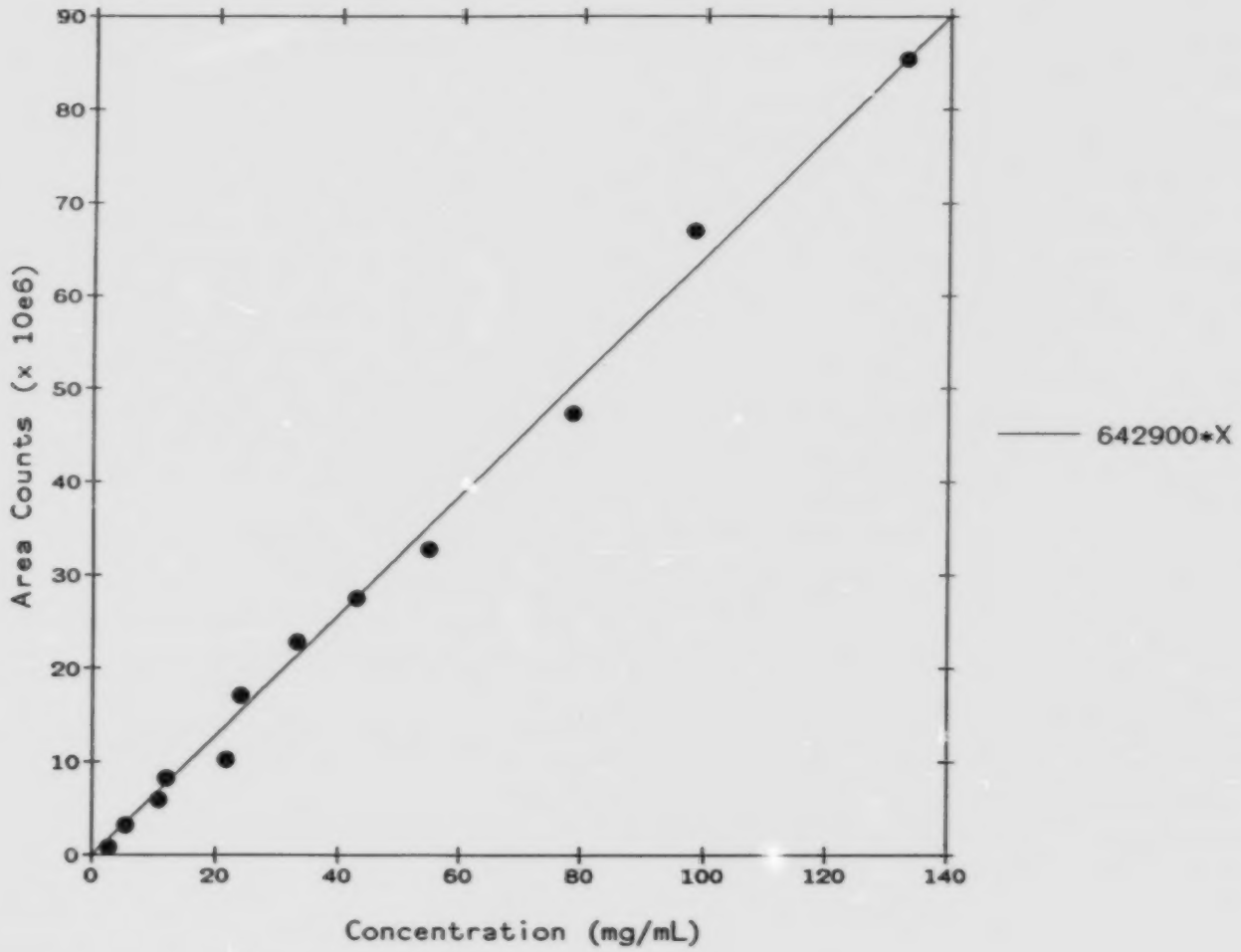
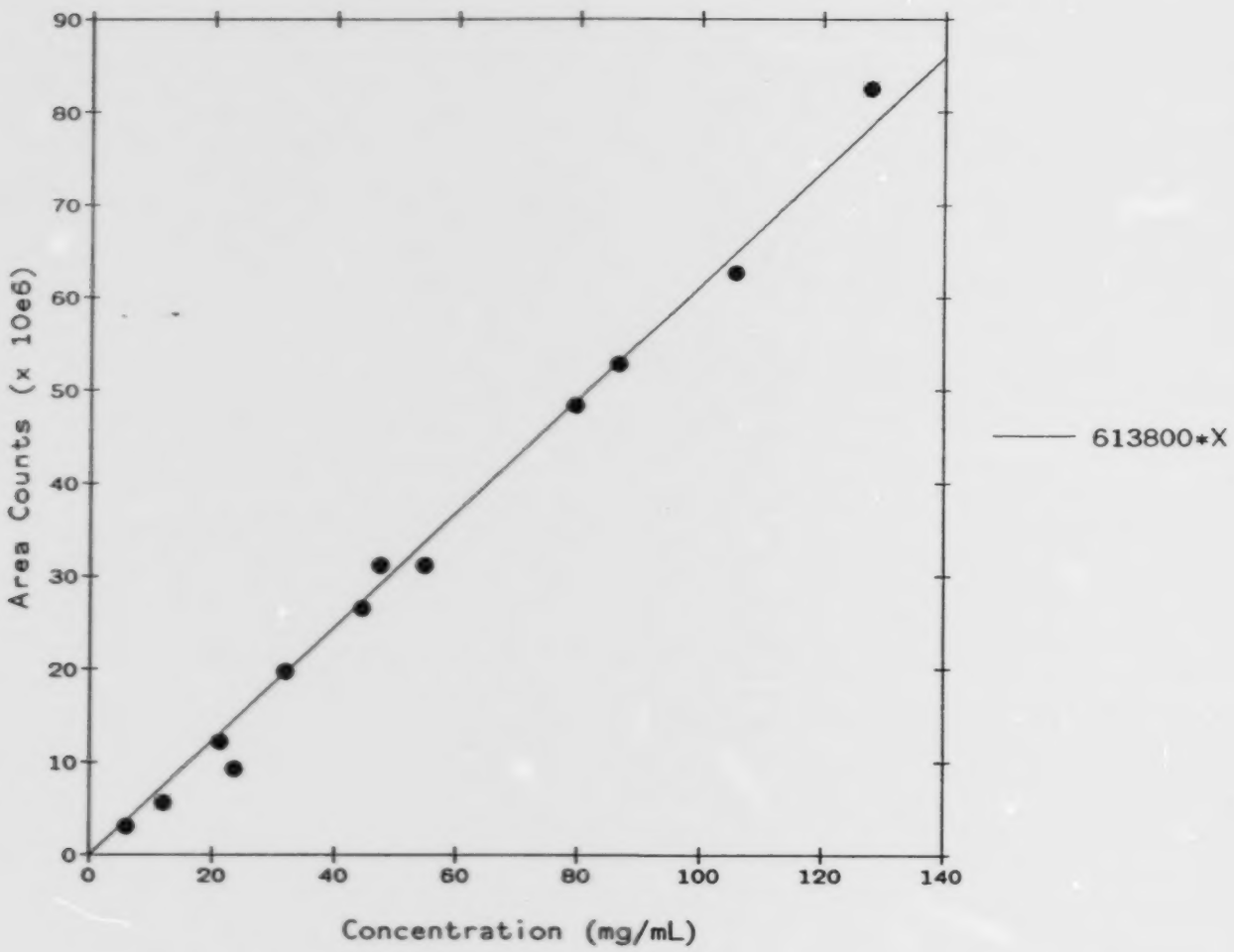


Figure 12: Saturates calibration curve over the linear range



0	1 Conc	2 Area
1	24.0	17061540
2	12.0	8221363
3	42.9	27495592
4	21.7	10230583
5	10.8	5954428
6	5.4	3173073
7	2.7	780001
8	98.1	67044586
9	54.8	32733902
10	78.4	47316766
11	132.9	85390777
12	33.2	22809408

Figure 13: Aromatics calibration curve over the linear range



0	1 Conc	2 Area
1	54.7	31131364
2	31.9	19726121
3	127.9	82509597
4	47.4	31126183
5	12.0	5616485
6	6.0	3040723
7	23.6	9216817
8	79.5	48423923
9	21.2	12151263
10	44.4	26497852
11	86.6	52911789
12	105.7	62739946

Figure 14: Comparison of calibration curves

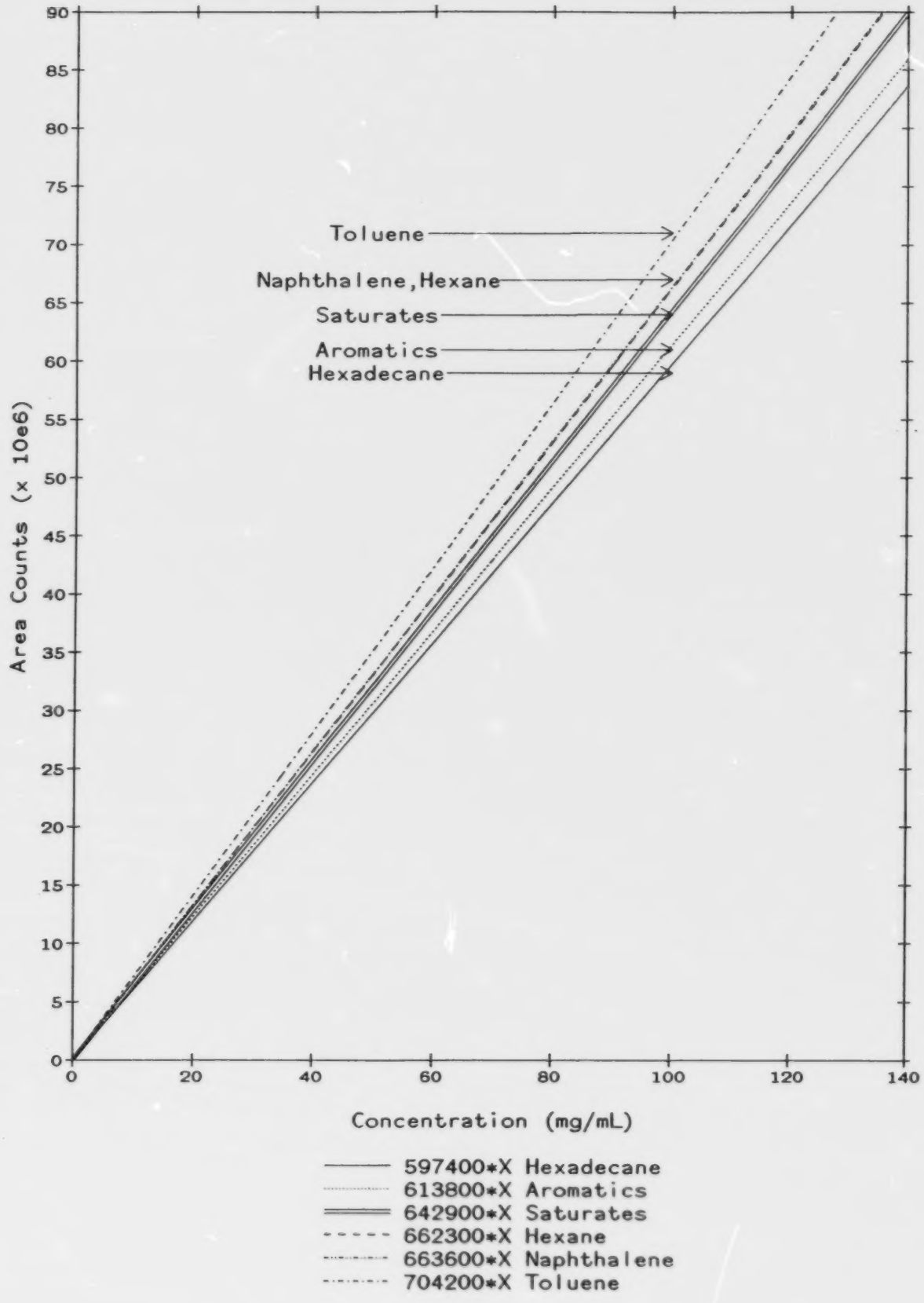


Figure 15: Comparison of aromatics content by SFC and FIA

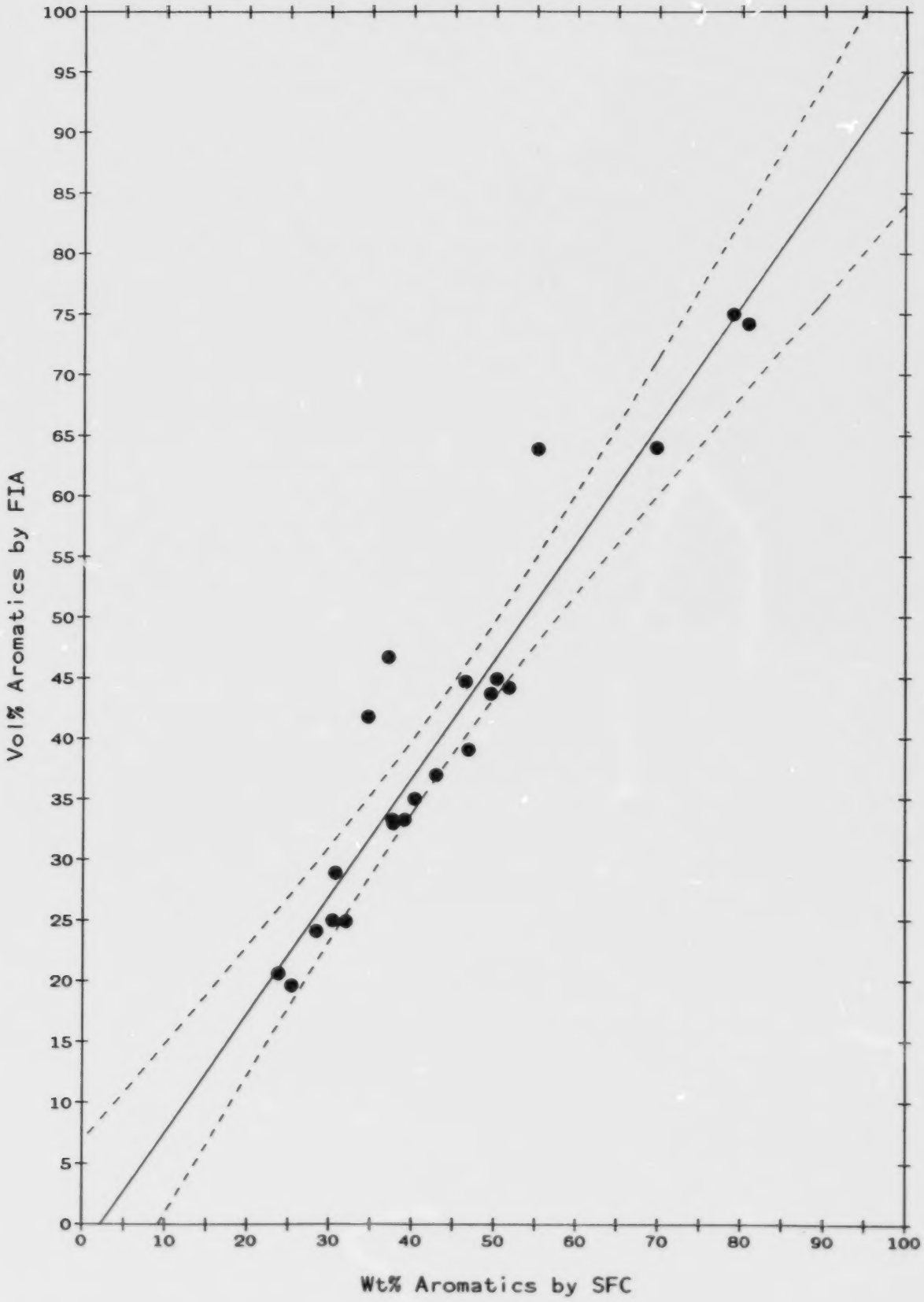


Figure 16: Comparison of aromatics content by SFC and NMR

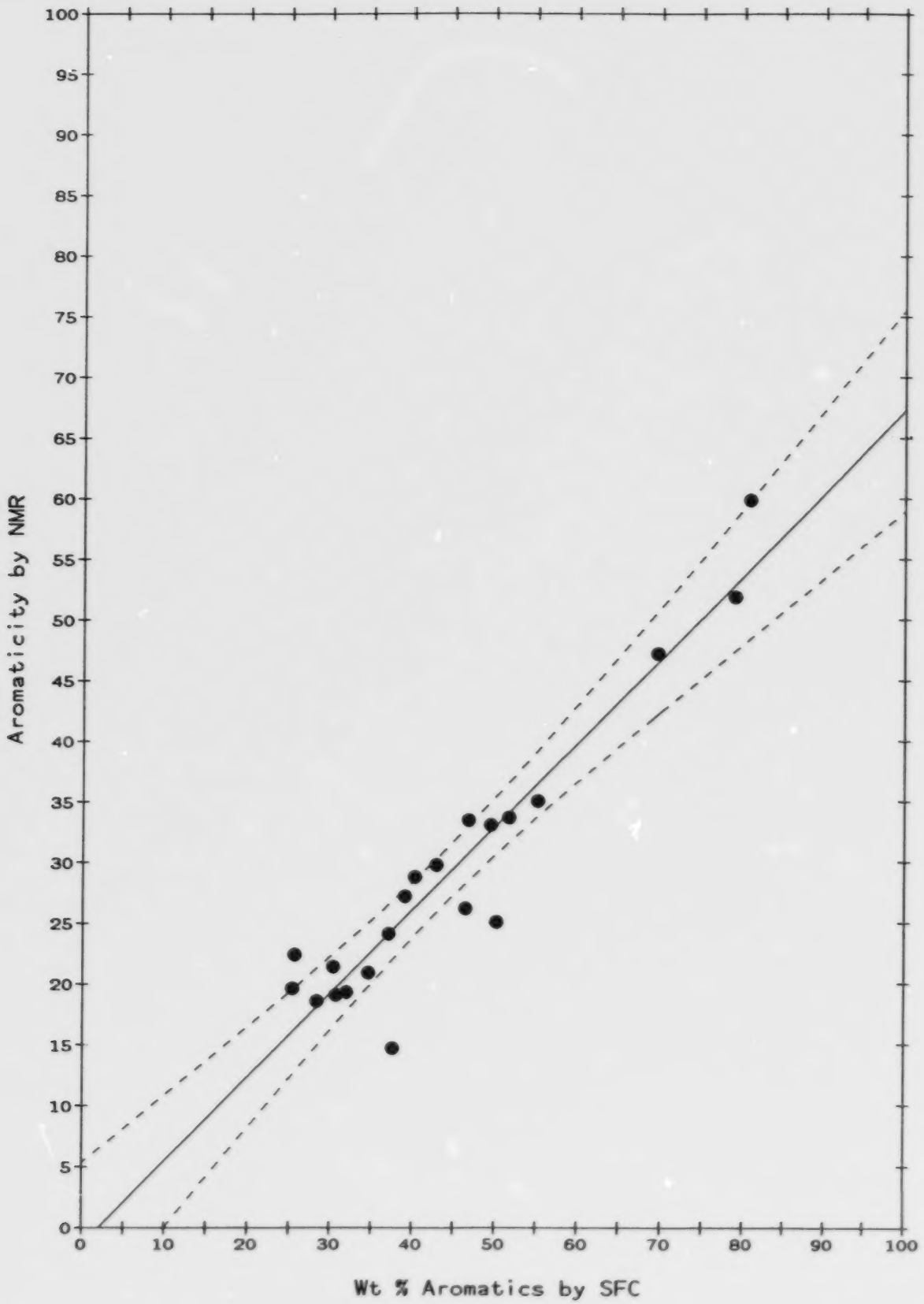


Figure 17: Comparison of aromatics content by SFC and MS/NMR

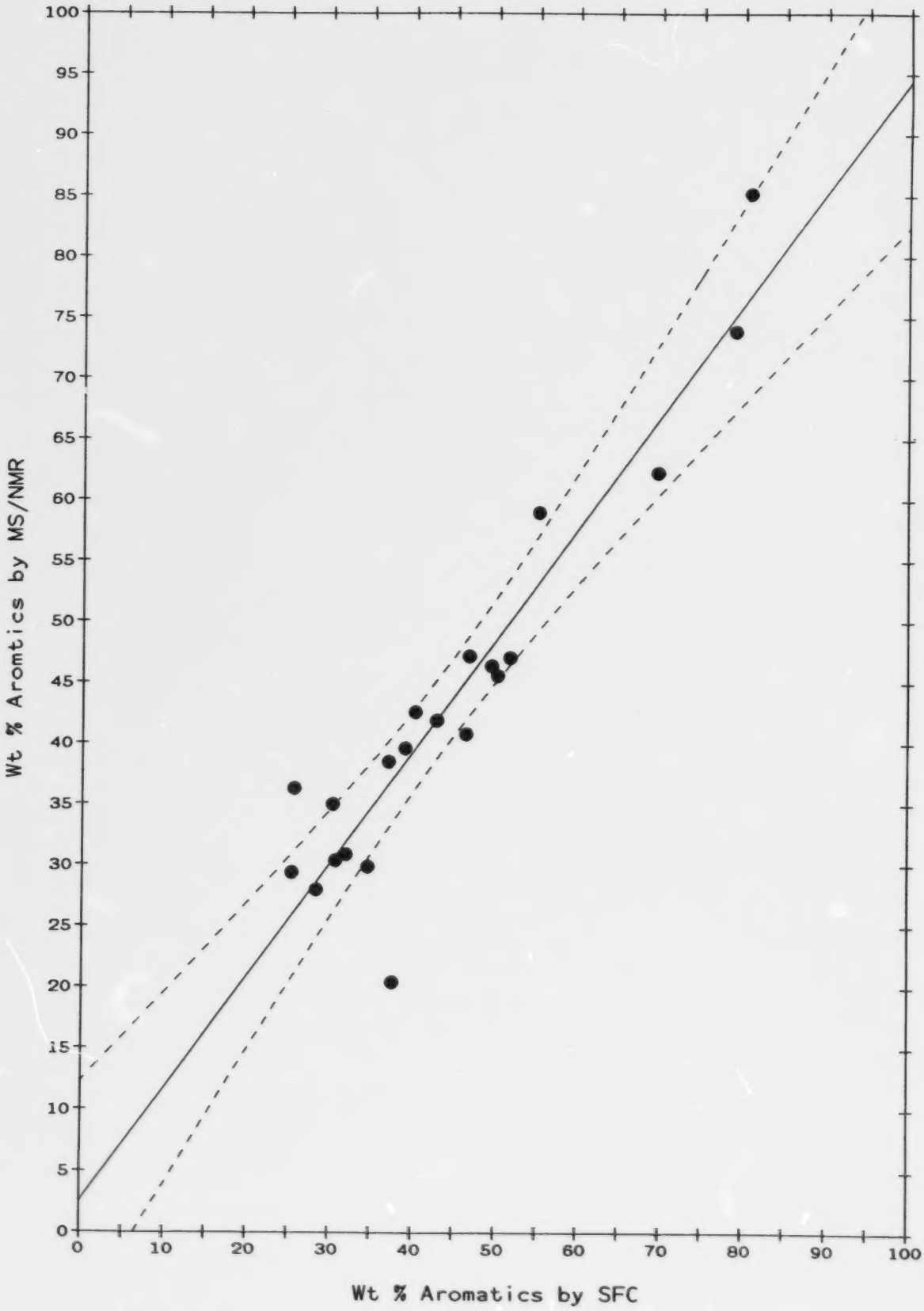


Figure 18 : SFC chromatograms of sample ST-11 and of its saturates, mono-, di-, and polyaromatics fractions after separation by column chromatography.

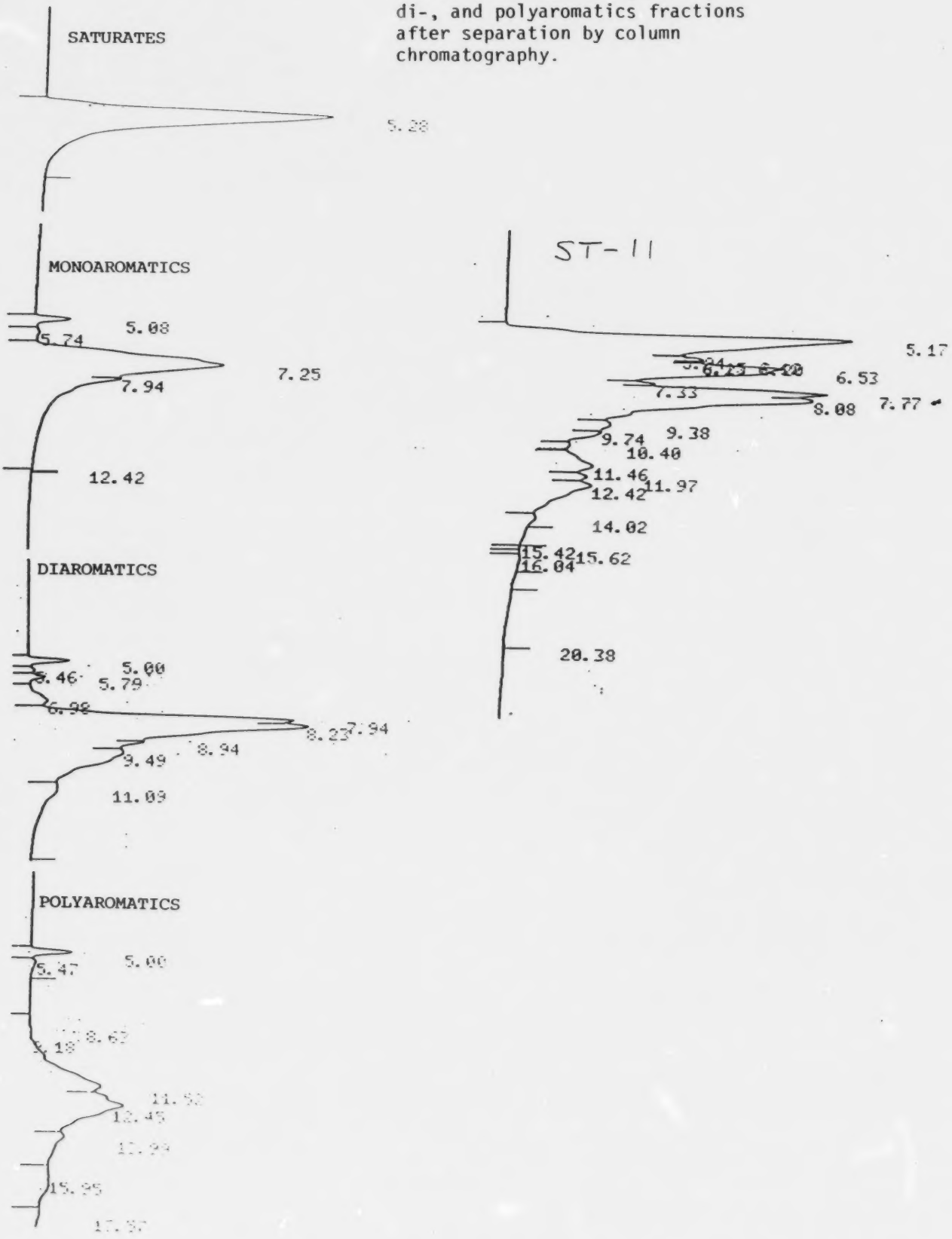
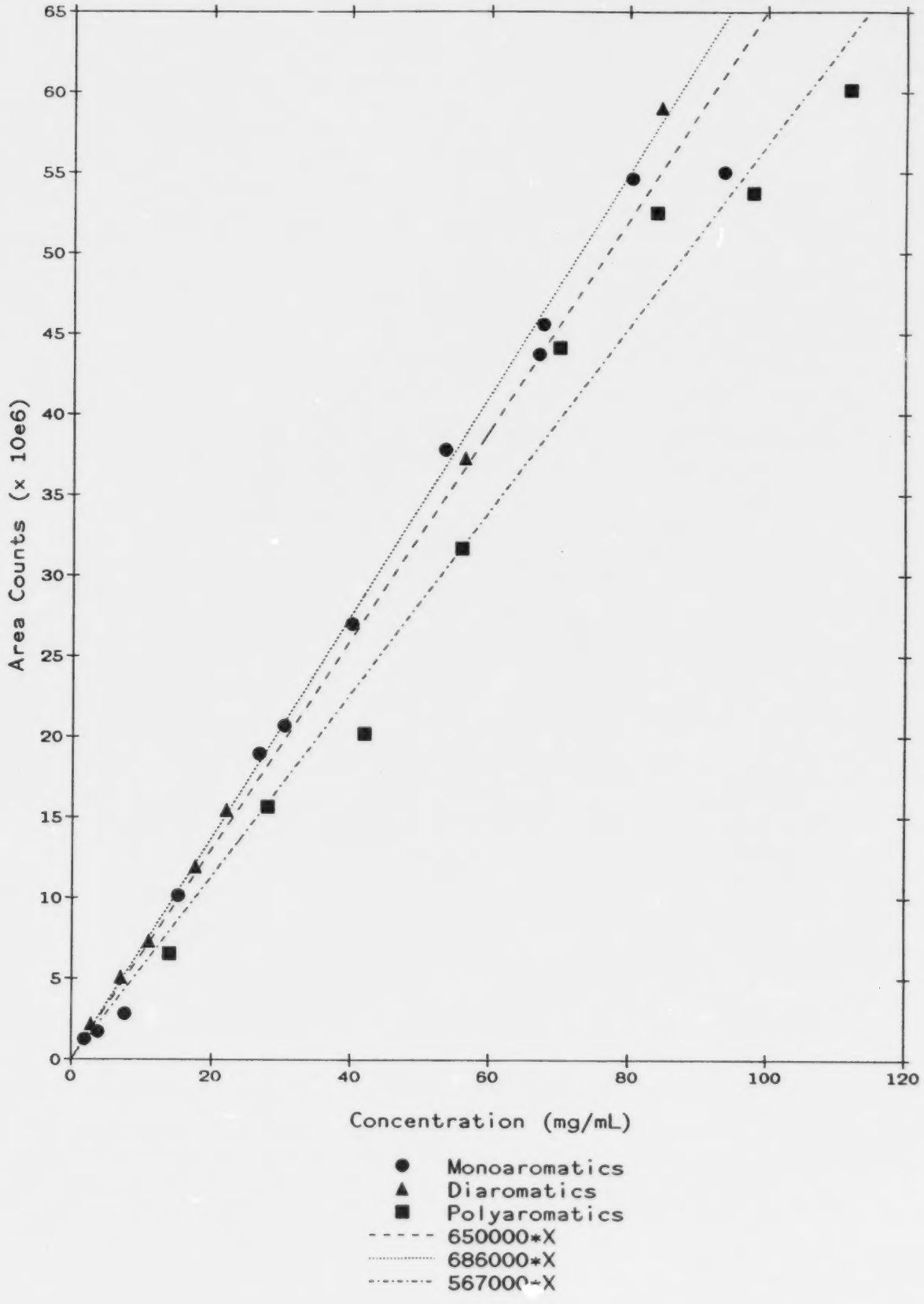


Figure 19: Calibration curves for mono-, di- and polyaromatics



APPENDIX 1

Simulated Distillation Data (D 2887) for Diesel and Middle Distillate Samples*

Sample	Temperature (°C)				
	IBP	10%	50%	90%	FBP
8	114	166	261	331	379
102	214	266	292	313	343
103	220	294	334	374	396
185	118	283	329	369	396
187	117	162	265	340	387
281	120	172	275	331	386
284	135	180	239	288	361
3200	126	176	249	319	376
3256	187	248	298	341	368
3259	162	220	281	328	372
LAD	113	157	199	254	371
HAD	172	231	274	318	366
ST-3	100	118	170	230	340
ST-4	123	181	234	300	384
ST-6	143	209	273	333	411
ST-7	135	190	274	367	437
ST-8	140	203	276	345	432
ST-10	147	210	286	379	447
ST-11	164	218	291	385	450
ST-12	140	194	261	319	395
ST-14	145	212	268	326	398

* Data provided by Scientific Authority

APPENDIX 2

SFC/FID Calibration Data for Some Pure Compounds*

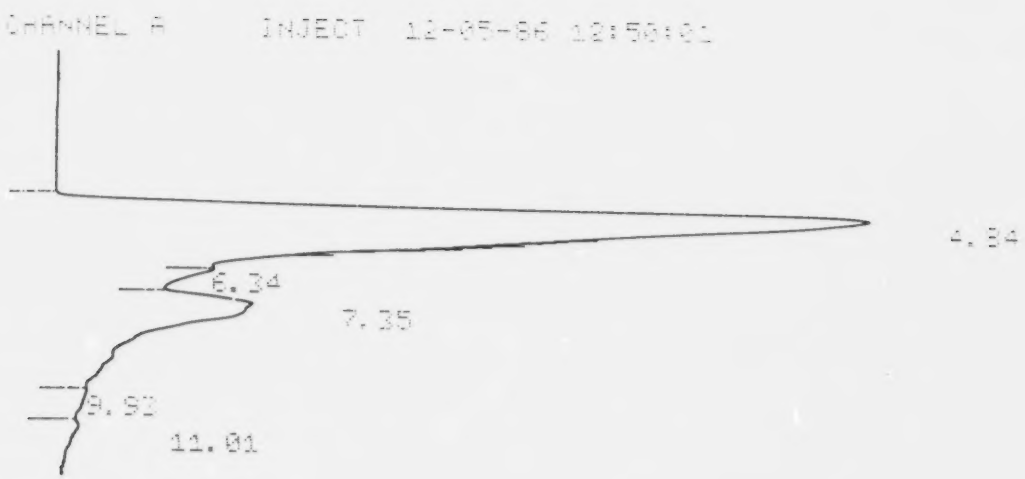
	Concentration (μg/μL)	Area Counts
Hexane	33.0	21834000
	13.2	9160000
	6.6	4126000
Hexadecane	39.8	22966554
	30.2	18157884
	30.2	17931408
	19.8	11455903
	19.8	11924039
	10.2	6052524
	10.2	5941024
	50.0	29835408
	33.3	20767439
	25.0	15506886
Toluene	8.7	6107081
	17.3	11985259
	43.4	30722667
Naphthalene	10.2	6501471
	20.2	13429782
	20.2	13518585
	30.1	19520084
	30.1	20049191
	40.2	27620702
	40.2	28165082
	50.0	31456920
	33.3	22063893
	25.0	16436482

* Conditions were 3250 psi and 90°C.

APPENDIX 3

SFC Chromatograms of All Diesel and Middle Distillate Samples
at 3250 psi and 90°C

Figure A3-1: Sample 8

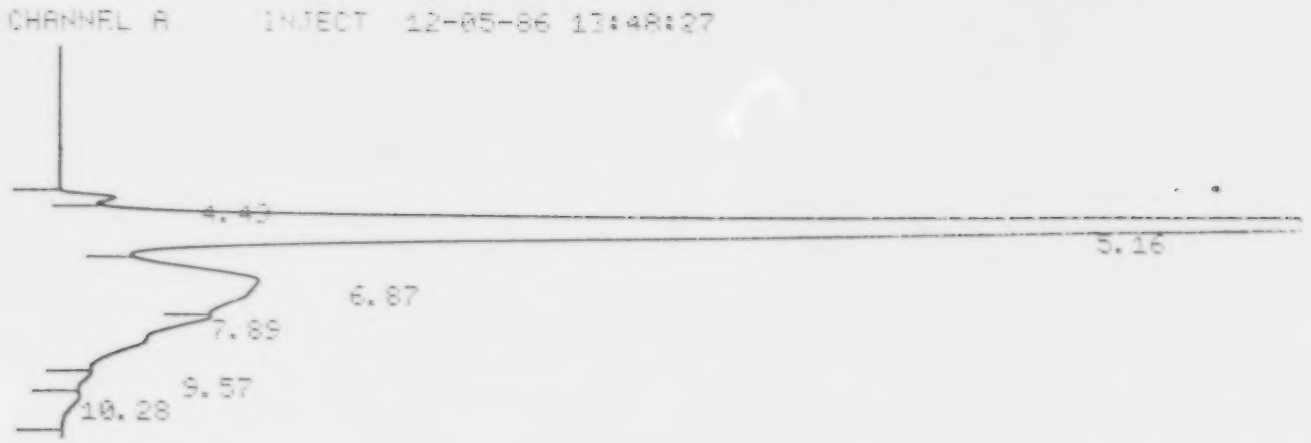


12-05-86 12:50:01 CH= "A" PG= 1.

FILE 1. METHOD 0. RUN 317 INDEX 317

PEAK#	AREA%	RT	AREA #C
1	69.771	4.84	43121445 02
2	6.536	6.34	4039218 02
3	21.102	7.35	13042156 02
4	1.553	9.93	960046 02
5	1.038	11.01	641229 02
TOTAL	100.		61804094

Figure A3-2: Sample 102

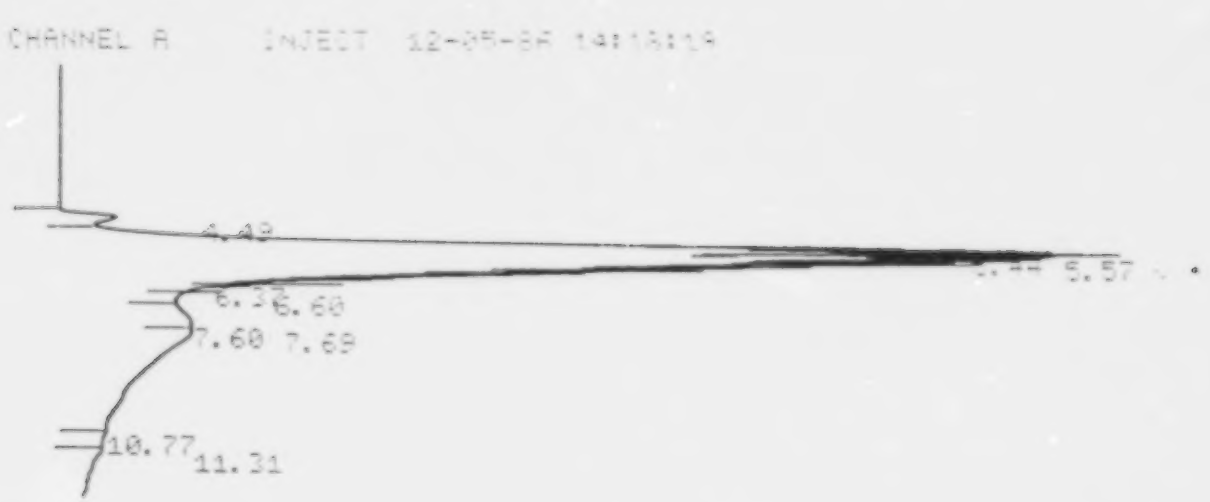


12-05-86 13:48:27 CH= "A" PS=

FILE 1. METHOD 0. RUN 321 INDEX 321

PEAK#	AREA%	RT	AREA BC
1	0.931	4.49	648531 02
2	69.799	5.16	48625820 02
3	18.353	6.87	12786092 02
4	9.333	7.89	6501815 02
5	0.931	9.57	648528 02
6	0.653	10.28	455034 02
TOTAL	100.		69665820

Figure A3-3: Sample 103

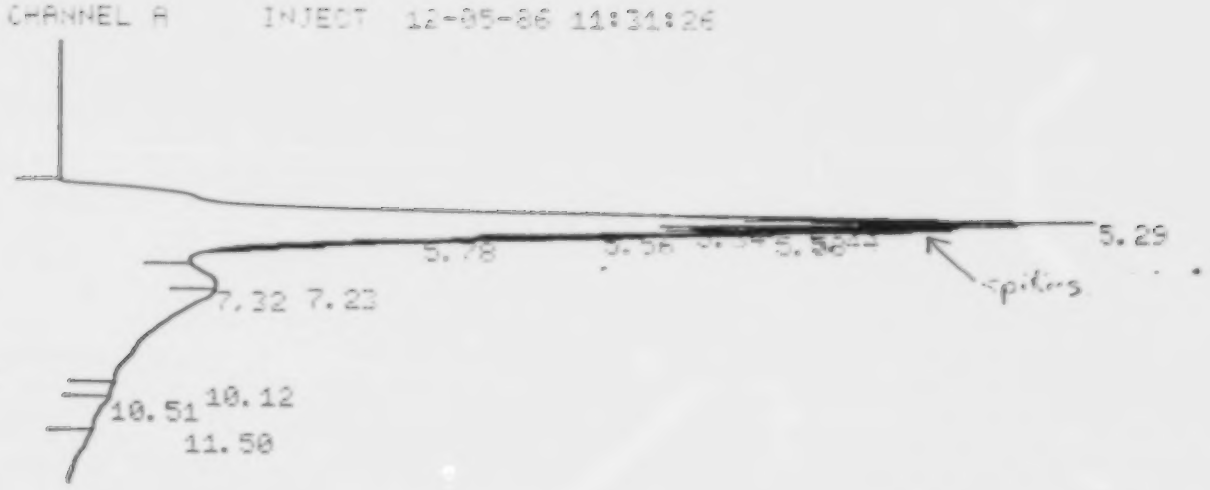


12-05-86 14:18:19 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 323 INDEX 323

PEAK#	AREA%	RT	AREA	BC
1	1.295	4.49	729667	02
2	24.127	5.44	13589882	02
3	41.165	5.57	23186357	02
4	2.998	6.27	1688836	02
5	3.267	6.6	1840336	02
6	6.916	7.6	3895701	02
7	17.943	7.69	10106781	02
8	0.993	10.77	559381	02
9	1.294	11.31	728912	02
TOTAL	100.		56325853	

Figure A3-4: Sample 185

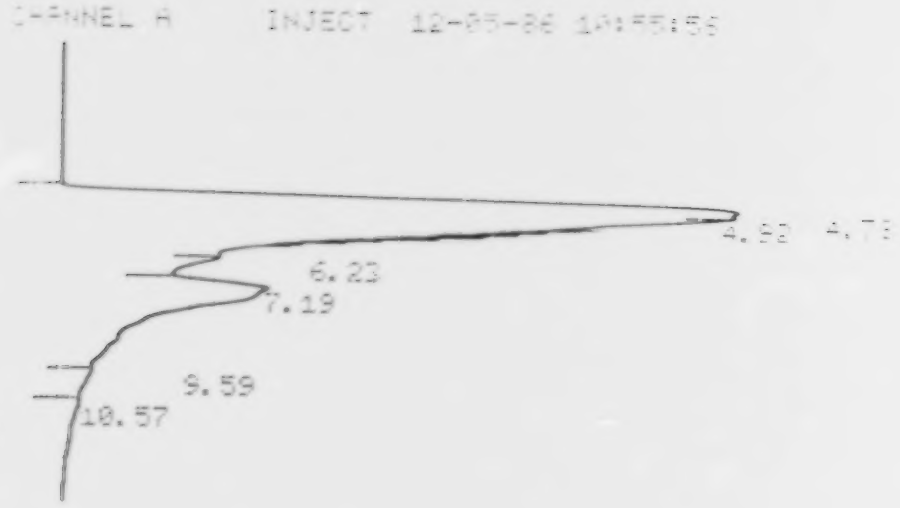


12-05-86 11:31:26 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 311 INDEX 311

PEAK#	AREA%	RT	AREA	BC
1	25.338	5.29	14988336	02
2	7.137	5.34	4221645	02
3	8.93	5.44	5282695	02
4	1.016	5.56	601228	02
5	9.625	5.58	5693270	02
6	13.657	5.78	8078381	02
7	8.431	7.23	4986974	02
8	20.277	7.32	11994545	02
9	1.484	10.12	878039	02
10	2.685	10.51	1587989	02
11	1.421	11.5	840685	03
TOTAL	100.		59153787	

Figure A3-5: Sample 187

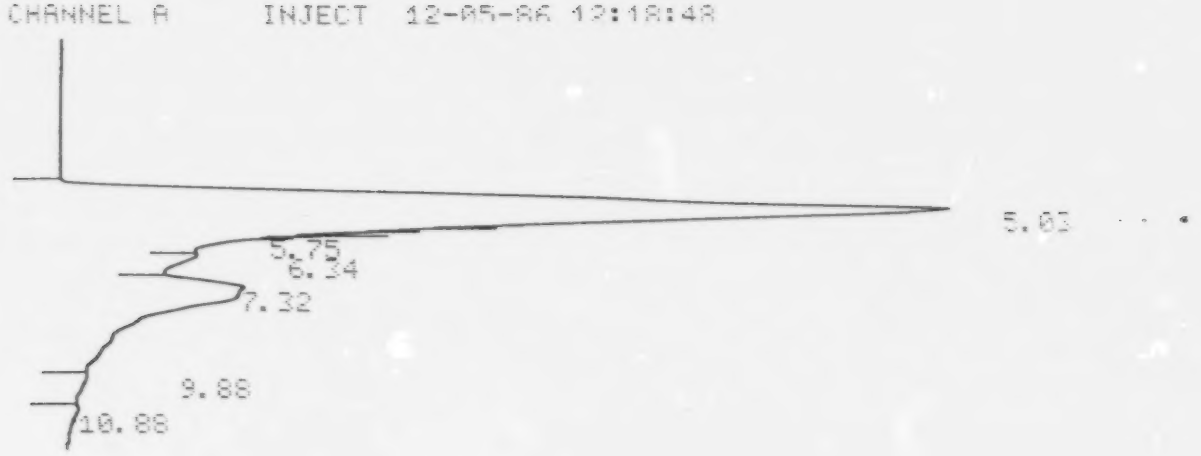


12-05-86 10:55:56 CH= "A" FS= 1.

FILE 1. METHOD 0. RUN 309 INDEX 309

PEAK#	AREA%	RT	AREA	BC
1	24.77	4.78	13975969	02
2	41.874	4.92	23626557	02
3	6.661	6.22	3758387	02
4	23.261	7.19	13124568	02
5	1.719	9.59	969961	02
6	1.716	10.57	96R171	03
TOTAL	100.		56423613	

Figure A3-6: Sample 281



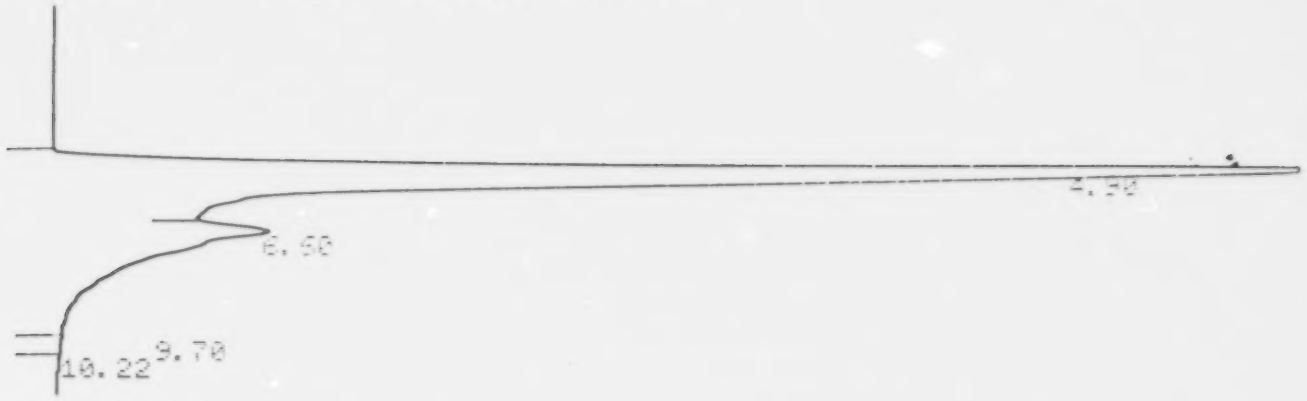
12-05-86 12:18:48 CH= "A" FS= 1.

FILE 1. METHOD 0. RUN 315 INDEX 315

PEAK#	AREA%	RT	AREA	BC
1	63.185	5.03	35877240	02
2	7.139	5.75	4053555	02
3	6.486	6.34	3683108	02
4	21.268	7.32	12076329	02
5	1.284	9.88	729207	02
6	0.638	10.88	362057	03
TOTAL	100.		56781496	

Figure A3-7: Sample 284

CHANNEL A INJECT 12-05-86 13:20:11

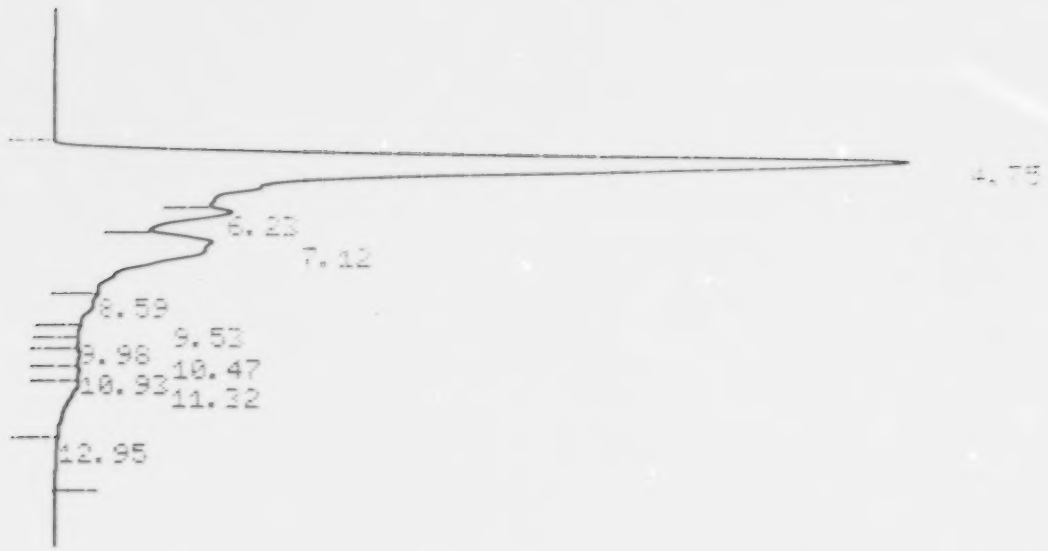


12-05-86 13:20:11 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 319 INDEX 319

PEAK#	AREA%	RT	AREA BC
1	77.735	4.9	42782500 02
2	21.899	6.6	12052174 02
3	0.223	9.7	122890 02
4	0.143	10.22	78608 03
TOTAL	100.		55036172

Figure A3-8: Sample 3200

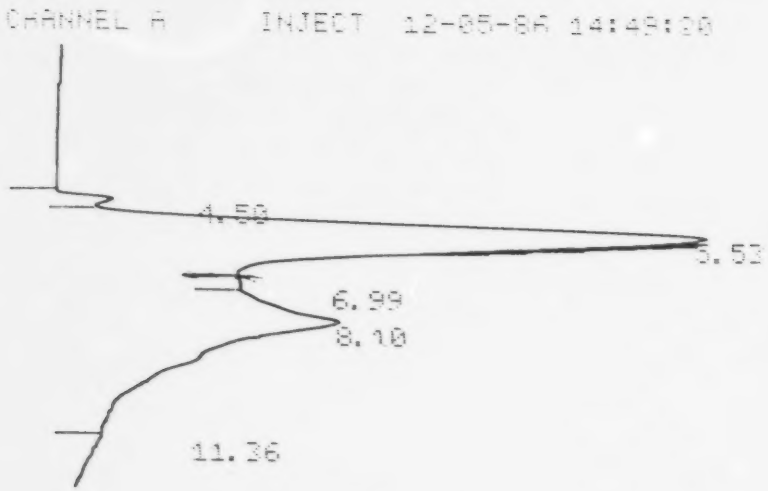


12-05-86 10:00:43 CH= "A" PG= 1.

FILE 1. METHOD 0. RUN 306 INDEX 306

PEAK#	AREA%	RT	AREA	BC
1	63.701	4.75	31299598	02
2	9.883	6.23	4856125	02
3	17.229	7.12	8465561	02
4	3.269	8.59	1605810	02
5	0.792	9.53	389097	02
6	0.793	9.98	389520	02
7	1.182	10.47	580685	02
8	0.968	10.93	475499	02
9	1.977	11.32	971351	02
10	0.207	12.95	101777	03
TOTAL	100.		49135025	

Figure A3-9: Sample 3256

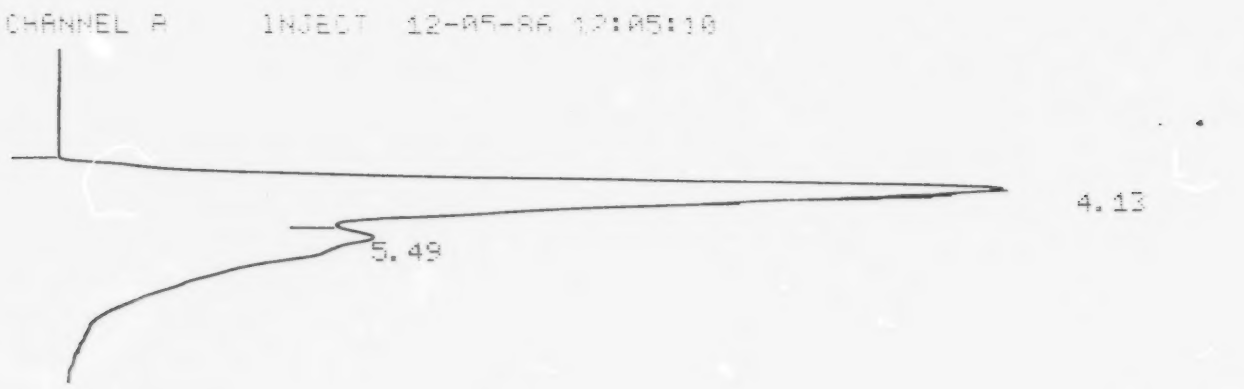


12-05-86 14:49:20 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 325 INDEX 325

PEAK#	AREA%	RT	AREA	BC
1	1.116	4.5	708158	02
2	50.208	5.53	31859898	02
3	5.482	6.99	3478835	02
4	41.269	8.1	26187508	02
5	1.925	11.36	1221368	03
TOTAL	100.		63455767	

Figure A3-10: Sample 3259

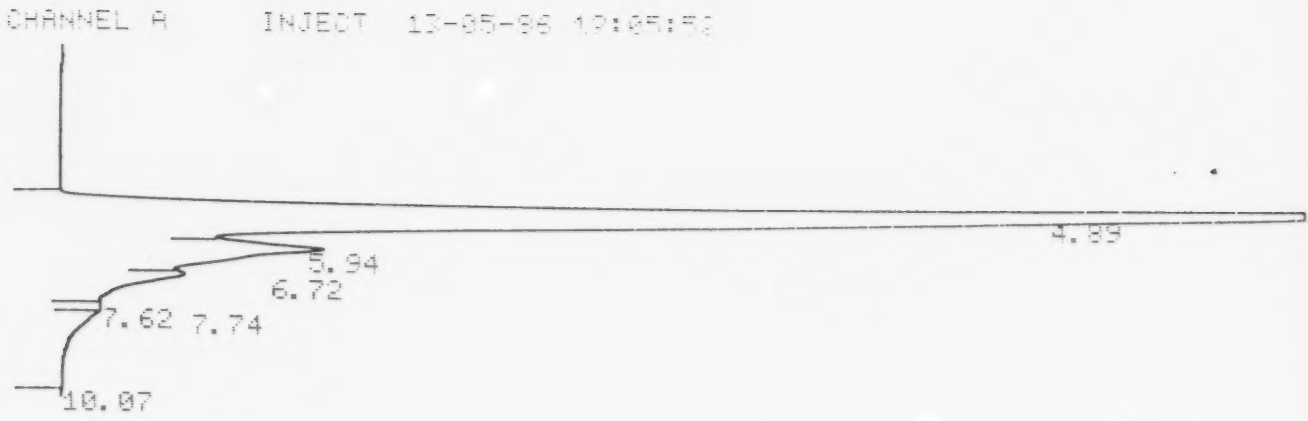


12-05-86 12:05:10 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 314 INDEX 314

PEAK#	AREA%	RT	AREA	RC
1	66.403	4.13	45213999	02
2	33.597	5.49	22876252	03
TOTAL	100.		68090251	

Figure A3-11: Sample LAD

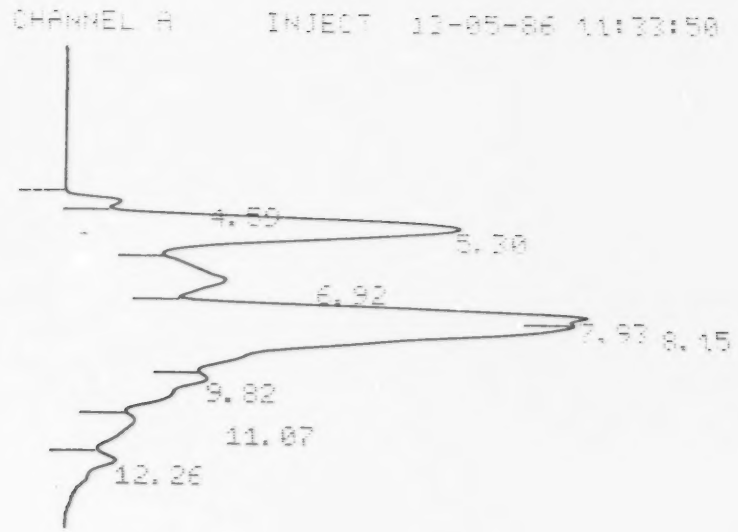


13-05-86 12:05:12 Chn 'A' Pos ...

FILE 1. METHOD 0. RUN 343 INDEX 343

PEAK#	AREA%	RT	AREA	BC
1	74.193	4.89	38697069	02
2	16.13	5.94	8413099	02
3	6.589	6.72	3436440	02
4	0.796	7.62	414961	02
5	2.289	7.74	1193728	02
6	0.004	10.07	2174	03
TOTAL	100.		52157471	

Figure A3-12: Sample HAD



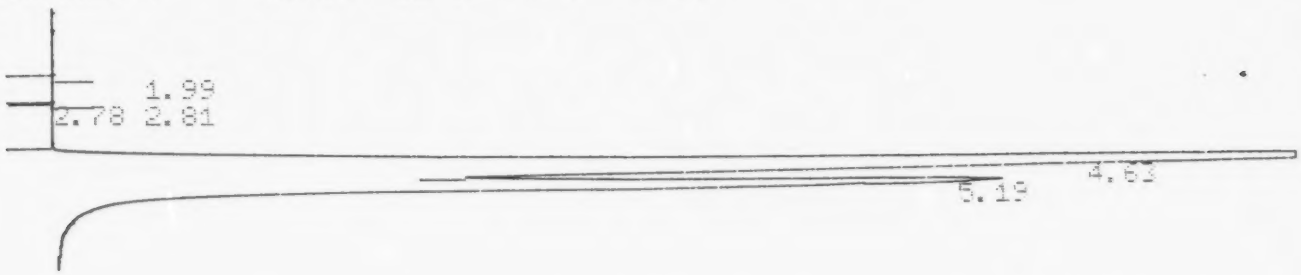
13-05-86 11:33:50 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 341 INDEX 341

PEAK#	AREA%	RT	AREA	BC
1	1.138	4.59	765422	02
2	22.304	5.3	14999831	02
3	11.922	6.92	8017596	02
4	16.613	7.93	11172240	02
5	31.451	8.15	21151083	02
6	9.24	9.82	6214252	02
7	4.415	11.07	2969141	02
8	2.916	12.26	1960689	03
TOTAL	100.		67250254	

Figure A3-13: Sample ST-3

CHANNEL A INJECT 21-05-86 10:59:26

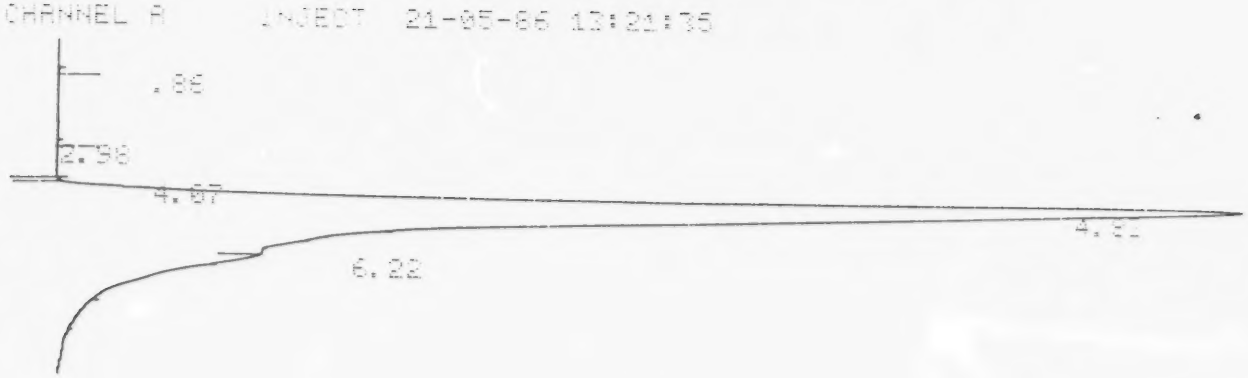


21-05-86 10:59:26 CH= "A" FS= 1.

FILE 1. METHOD 0. RUN 389 INDEX 389

PEAK#	AREA%	RT	AREA	BC
1	0.004	1.99	1759	01
2	0.003	2.78	1221	02
3	0.002	2.81	899	03
4	62.711	4.63	28567696	02
5	37.281	5.19	16983245	03
TOTAL	100.		45554820	

Figure A3-14: Sample ST-4

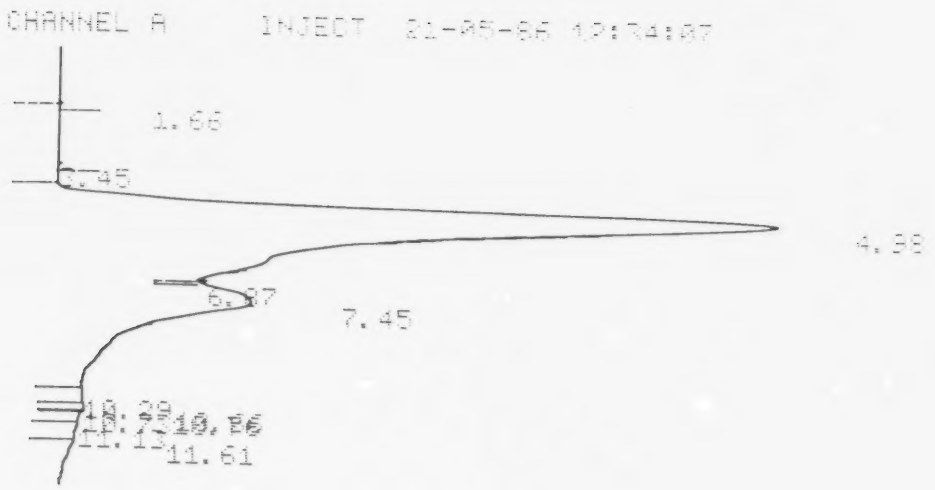


21-05-86 13:21:35 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 398 INDEX 398

PEAK#	AREA%	RT	AREA BC
1	0.006	0.86	3132 01
2	0.005	2.38	2951 01
3	0.013	4.07	6937 02
4	84.205	4.83	45962116 02
5	15.767	6.22	8605810 03
TOTAL	100.		54580946

Figure A3-15: Sample ST-6

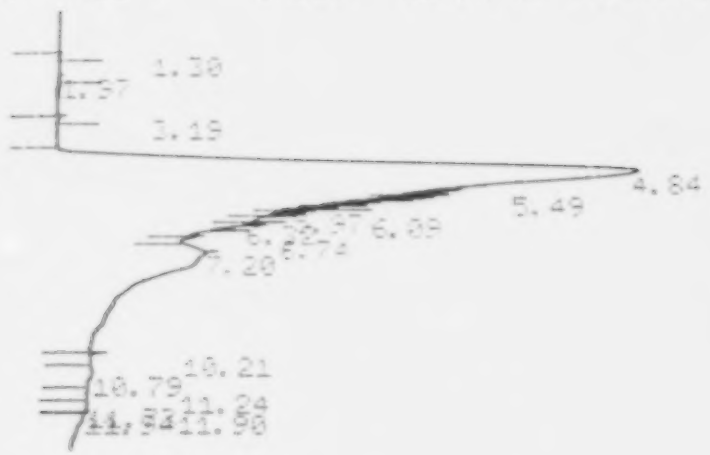


21-05-86 12:34:07 CH= "A" FS= 1.

FILE 1. METHOD 0. RUN 395 INDEX 395

PEAK#	AREA%	RT	AREA BC
1	0.004	1.66	2163 01
2	0.007	3.45	3708 01
3	72.082	4.98	40575168 02
4	0.994	6.87	559409 02
5	23.5	7.45	13228418 02
6	0.927	10.29	521782 02
7	0.406	10.56	228365 02
8	0.067	10.73	37871 02
9	0.523	10.76	294554 02
10	0.76	11.13	428012 02
11	0.73	11.61	410834 03

Figure A3-16: Sample ST-7

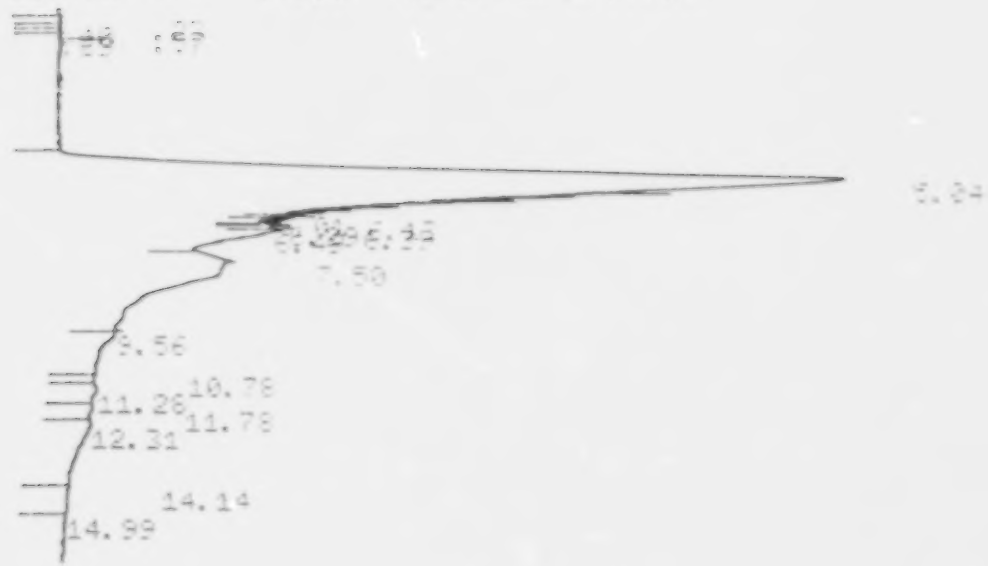


21-05-86 11:57:01 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 392 INDEX 392

PEAK#	AREA%	RT	AREA	BC
1	0.009	1.3	4414	01
2	0.01	1.97	5067	01
3	0.014	3.19	7299	01
4	44.697	4.84	22609827	02
5	12.955	5.49	6553405	02
6	3.494	5.97	1767347	02
7	3.596	6.09	1818931	02
8	6.977	6.32	3527125	02
9	2.539	6.74	1284509	02
10	21.352	7.2	10800678	02
11	0.83	10.21	419887	02
12	1.368	10.79	692099	02
13	0.714	11.24	361203	02
14	0.605	11.72	306006	02
15	0.053	11.9	26937	02
16	0.791	11.94	400036	03
TOTAL	100.		50584779	

Figure A3-17: Sample ST-8



21-05-86 07:41:40 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 375 INDEX 375

PEAK#	AREA%	RT	AREA BC
1	0.003	0.33	2213 02
2	0.002	0.4	1468 02
3	0.002	0.57	1179 02
4	0.005	0.69	3329 02
5	54.658	5.04	34777916 02
6	1.612	6.01	1024483 02
7	3.077	6.13	1955148 02
8	0.772	6.29	490775 02
9	1.714	6.39	1088983 02
10	9.056	6.49	5754625 02
11	19.176	7.5	12185740 02
12	3.889	9.56	2471455 02
13	0.591	10.78	375551 02
14	1.462	11.26	929530 02
15	1.054	11.78	669661 02
16	2.495	12.31	1585485 02
17	0.304	14.14	193408 02
18	0.127	14.99	80908 02
TOTAL	100.		63547811

Figure A3-18: Sample ST-10

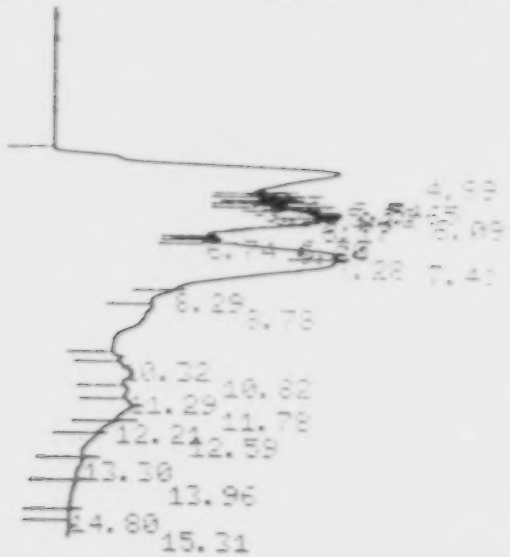
CHANNEL A INJECT 21-05-86 08:21:24

21-05-86 08:21:24 CH= "A" F#= _

FILE 1. METHOD 0. RUN 377 INDEX 377

PEAK#	AREA%	RT	AREA BC
1	29.594	5.01	16926392 02
2	0.869	5.59	497264 02
3	0.88	5.62	503598 02
4	1.263	5.71	722222 02
5	2.293	5.74	1311723 02
6	0.55	5.84	314425 02
7	0.849	5.87	485745 02
8	1.876	5.9	1072726 02
9	0.812	5.99	464556 02
10	2.121	6.08	1212928 02
11	3.066	6.21	1753601 02
12	1.198	6.29	685252 02
13	10.01	6.35	5725501 02
14	1.821	7.01	1041364 02
15	23.044	7.58	13180108 02
16	7.371	8.92	4215735 02
17	0.962	10.27	550477 02
18	4.126	11.31	2359637 02
19	1.641	11.84	938675 02
20	3.903	12.26	2232208 02
21	0.812	13.34	464440 02
22	0.387	14.06	221335 02
23	0.475	14.34	271699 02
24	0.077	15.29	43961 02
TOTAL	100.		57195561

Figure A3-19: Sample ST-11

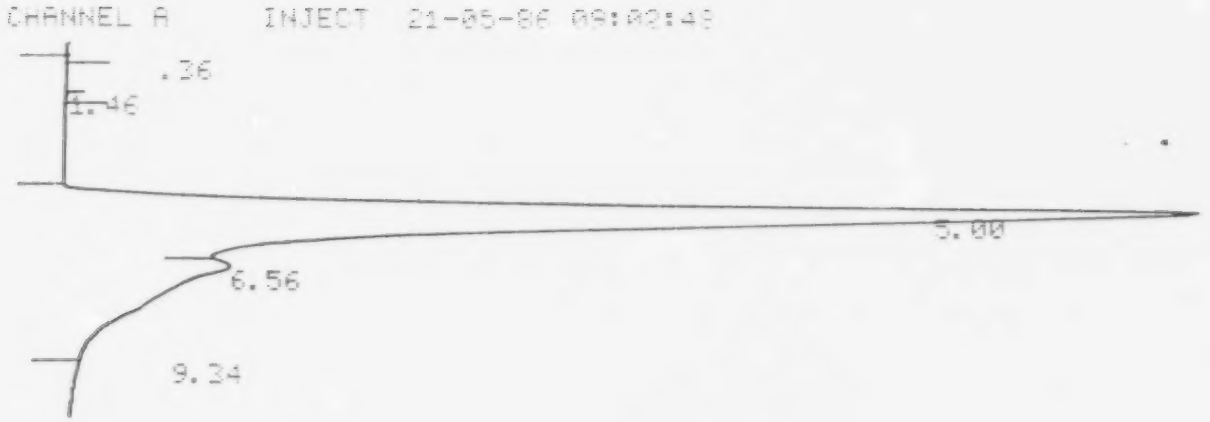


21-05-86 11:14:34 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 390 INDEX 390

PEAK#	AREA%	RT	AREA	BC
1	18.176	4.89	9974120	02
2	1.803	5.44	989224	02
3	2.169	5.54	1190209	02
4	0.468	5.62	256943	02
5	0.476	5.69	261263	02
6	0.779	5.69	427554	02
7	1.908	5.72	1047107	02
8	2.12	5.86	1163529	02
9	4.972	6.09	2729035	02
10	10.728	6.17	5886951	02
11	0.438	6.7	240597	02
12	0.874	6.74	479511	02
13	1.395	6.84	765301	02
14	8.079	7.28	4562400	02
15	16.86	7.41	9251852	02
16	3.554	8.29	1949174	02
17	8.848	8.78	4855414	02
18	1.33	10.22	729782	02
19	3.966	10.82	2177569	02
20	2.177	11.29	1192454	02
21	3.51	11.79	1926198	02
22	1.462	12.21	802497	02
23	1.483	12.59	813574	02
24	0.856	13.1	469798	02
25	0.433	13.96	237712	02
26	0.071	14.8	38953	02
27	0.068	15.21	37356	02
TOTAL	100.		54876108	

Figure A3-20: Sample ST-12

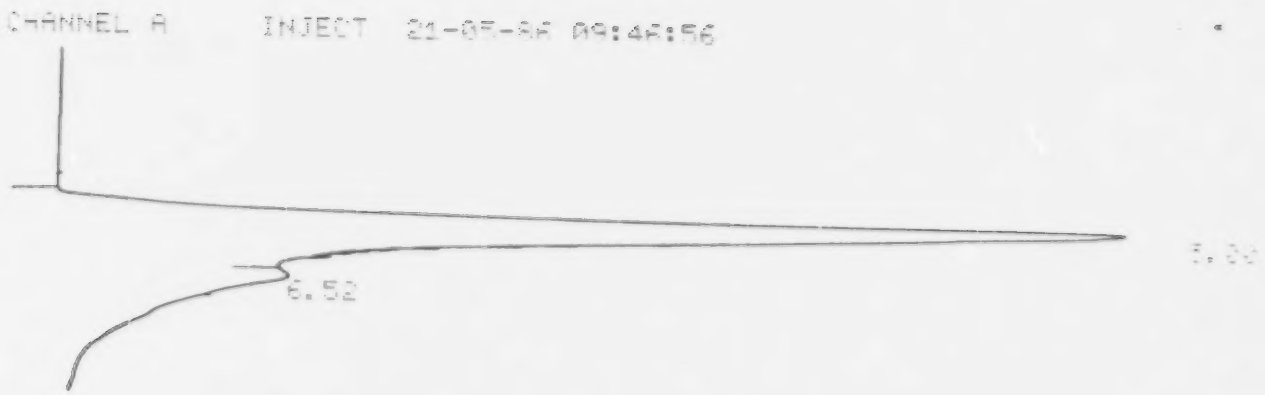


21-05-86 09:02:48 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 379 INDEX 379

PEAK#	AREA%	RT	AREA BC
1	0.007	0.36	3726 01
2	0.027	1.46	14863 01
3	79.291	5.	43751818 02
4	20.031	6.56	11052827 02
5	0.644	9.34	355596 03
TOTAL	100.		55178830

Figure A3-21: Sample ST-14

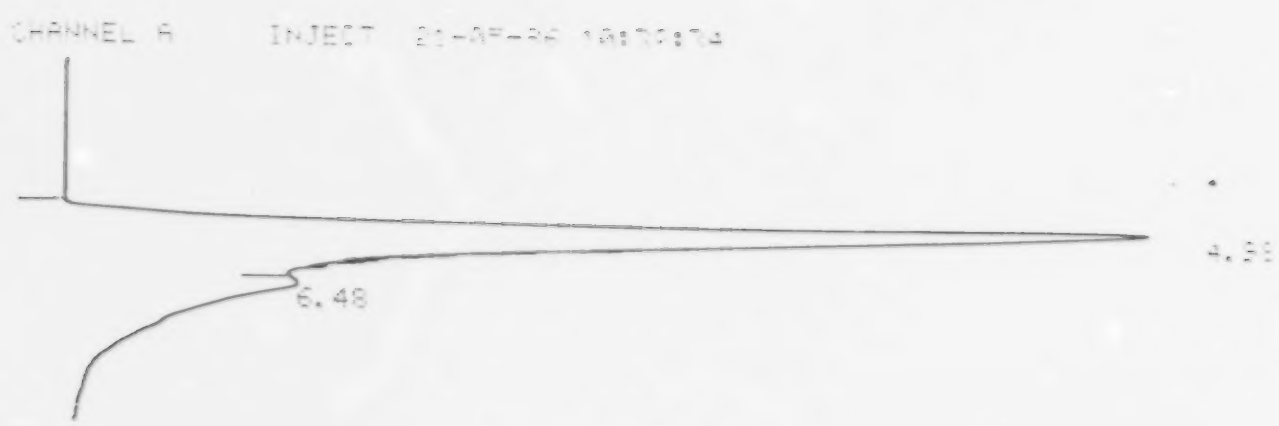


21-05-86 09:46:56 CH= "A" Fig= 1.

FILE 1. METHOD 0. RUN 382 INDEX 282

PEAK#	AREA%	RT	AREA #C
1	75.521	5.	47360821 02
2	24.479	6.52	14054797 02
TOTAL	100.		57415618

Figure A3-22: Sample ST-21



21-05-86 10:32:34 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 386 INDEX 386

PEAK#	AREA%	RT	AREA	BC
1	74.742	4.93	43542927	02
2	25.258	6.48	14714706	07
TOTAL	100.		58257643	

APPENDIX 4

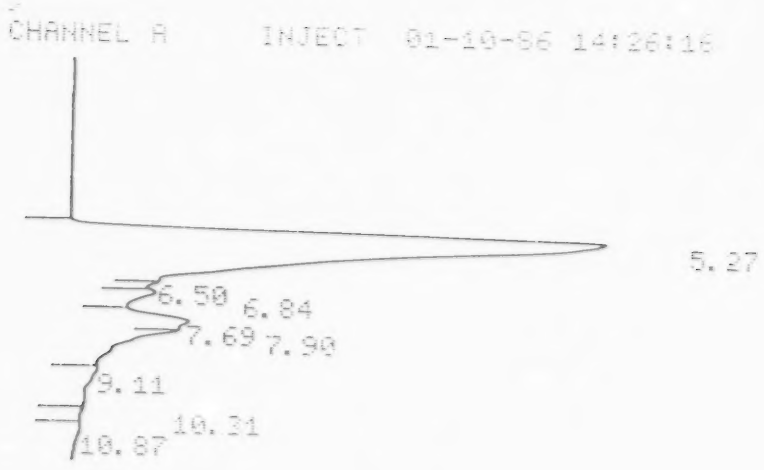
SFC Results of Each Analysis of Middle Distillates at 3250 psi and 90°C

Sample	Wt% Aromatics	Mean	Std Dev	%RSD
8	30.6, 29.8	30.2	0.6	2.0
102	29.4, 29.8	29.6	0.3	1.0
103	30.8, 31.9	31.4	0.8	2.6
185	35.7, 34.8	35.3	0.6	1.7
187	33.7, 33.8	33.8	0.1	0.3
281	30.1, 30.4	30.3	0.2	0.7
284	22.6, 22.8, 23.5, 20.1, 20.9, 21.5, 20.7, 20.1	21.7	1.2	5.5
3200	36.9, 37.3	37.1	0.3	0.8
3256	49.2, 49.5, 45.7, 46.3, 43.4, 46.9, 49.4, 47.7	47.3	2.1	4.4
3259	35.3, 34.0	34.7	0.9	2.6
LAD	25.4, 24.6	25.0	0.6	2.4
HAD	77.5, 77.4, 77.5, 77.5, 77.3, 77.4	77.4	0.1	0.1
ST-3	37.8, 38.0	37.9	0.1	0.3
ST-4	16.0, 16.0	16.0	0.0	0.0
ST-6	27.3, 28.4	27.9	0.8	2.9
ST-7	43.1, 41.7	42.4	0.9	2.1
ST-8	45.9, 45.5	45.7	0.3	0.7
ST-10	66.0, 67.1	66.6	0.8	1.2
ST-11	77.2, 79.0	78.1	1.3	1.7
ST-12	21.0, 20.8	20.9	0.1	0.5
ST-14	24.2, 24.8	24.5	0.5	2.0
ST-21	25.6, 27.0	26.3	1.0	3.8

APPENDIX 5

SFC Chromatograms of all Diesel and Middle Distillate Samples at 3600 psi and 90°C

Figure A5-1: Sample 8



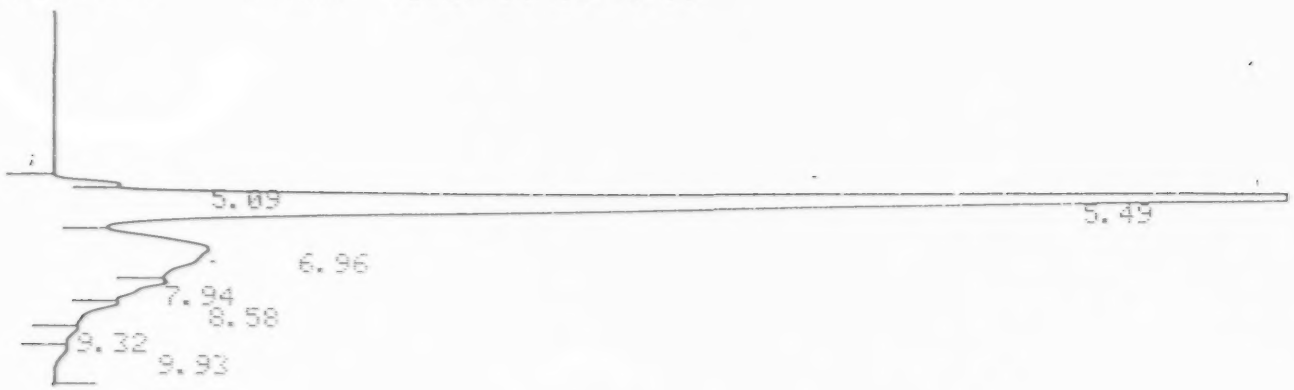
SYS 2 KEITHLY 01-10-86 14:26:16

FILE 1. METHOD 0. RUN 174 INDEX 174

PEAK#	AREA%	RT	AREA BC
1	68.978	5.27	22127616 02
2	2.714	6.5	870766 02
3	5.85	6.84	1876511 02
4	8.417	7.69	2700036 02
5	9.292	7.9	2980963 02
6	3.356	9.11	1076548 02
7	0.606	10.31	194423 02
8	0.787	10.87	252460 03
TOTAL	100.		32079323

Figure A5-2: Sample 102

CHANNEL A INJECT 01-10-86 15:48:50

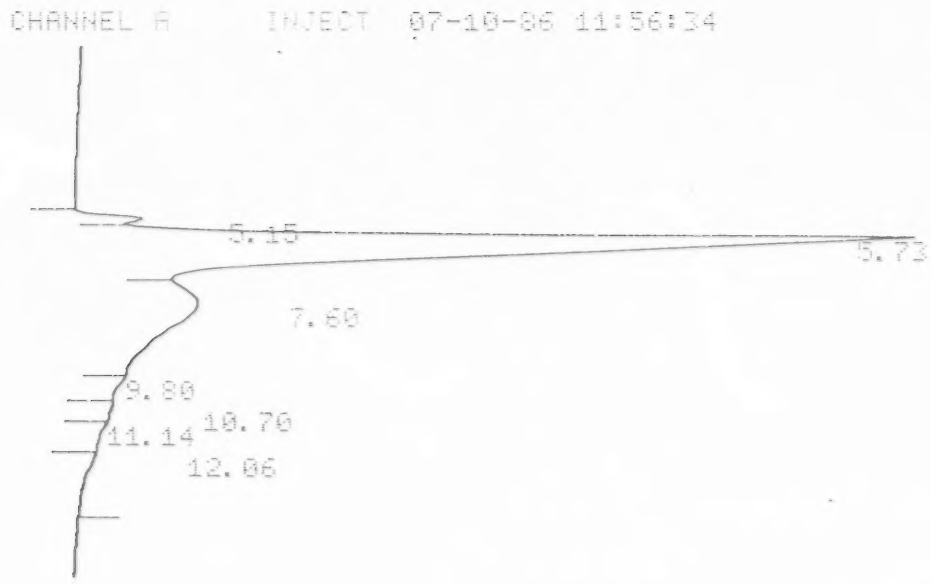


SYS 2 KEITHLY 01-10-86 15:48:50 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 180 INDEX 180

PEAK#	AREA%	RT	AREA	BC
1	1.24	5.09	586405	02
2	70.344	5.49	33255079	02
3	17.868	6.96	8447335	02
4	6.002	7.94	2837298	02
5	2.94	8.58	1390031	02
6	1.015	9.32	479982	02
7	0.59	9.93	279037	03
TOTAL	100.		47275167	

Figure A5-3: Sample 103

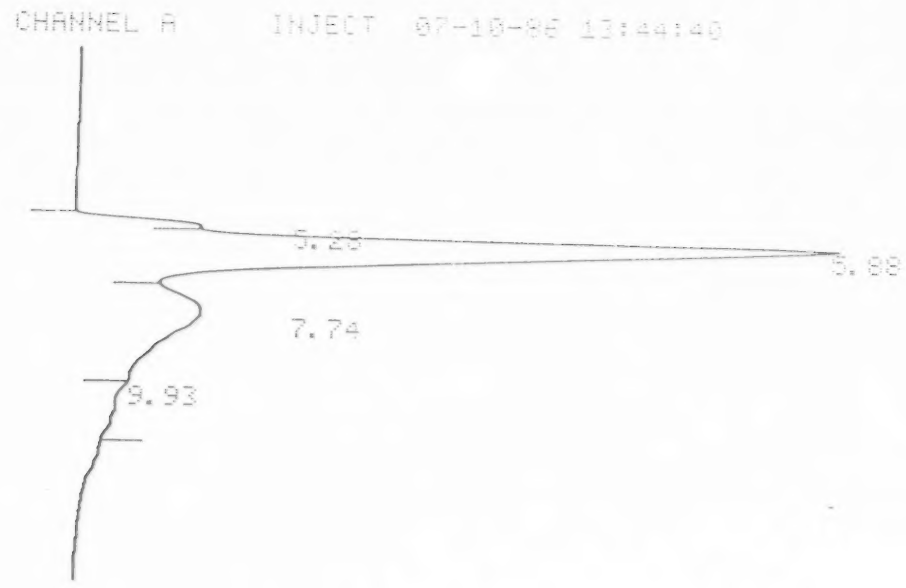


SYS 2 KEITHLY 07-10-86 11:56:34

FILE 1. METHOD 0. RUN 237 INDEX 237

PEAK#	AREA%	RT	AREA BC
1	1.738	5.15	773308 02
2	62.073	5.73	27623846 02
3	27.032	7.6	12029898 02
4	3.135	9.8	1395232 02
5	2.189	10.7	974018 02
6	2.308	11.14	1027096 02
7	1.525	12.06	678660 03
TOTAL	100.		44502058

Figure A5-4: Sample 185

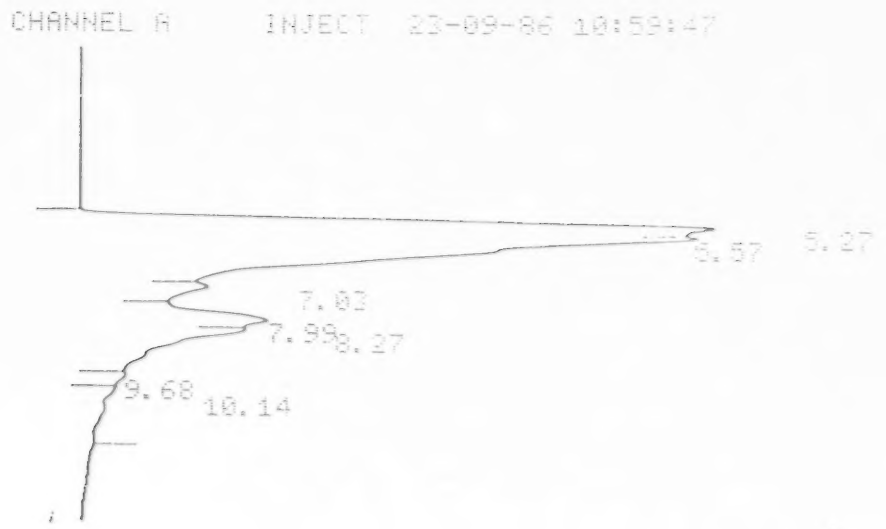


SYS 2 KEITHLY 07-10-86 13:44:40

FILE 1. METHOD 0. RUN 241 INDEX 241

PEAK#	AREA%	RT	AREA BC
1	3.974	5.28	1588971 02
2	66.38	5.88	26539510 02
3	26.322	7.74	10523747 02
4	3.324	9.93	1329116 03
TOTAL	100.		39981344

Figure A5-5: Sample 187

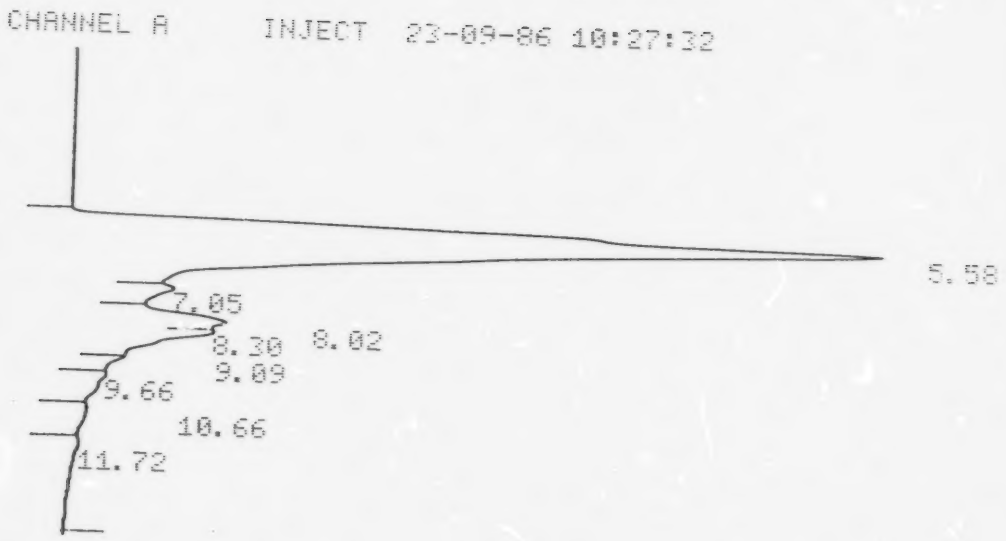


SYS 2 KEITHLY 23-09-86 10:59:47

FILE 1. METHOD 0. RUN 84 INDEX 84

PEAK#	AREA%	RT	AREA	BC
1	27.604	5.27	13530987	02
2	43.741	5.57	21441115	02
3	5.859	7.03	2871808	02
4	9.639	7.99	4725078	02
5	10.26	8.27	5029143	02
6	1.267	9.68	620857	02
7	1.632	10.14	799817	03
TOTAL	100.		49018805	

Figure A5-6: Sample 281

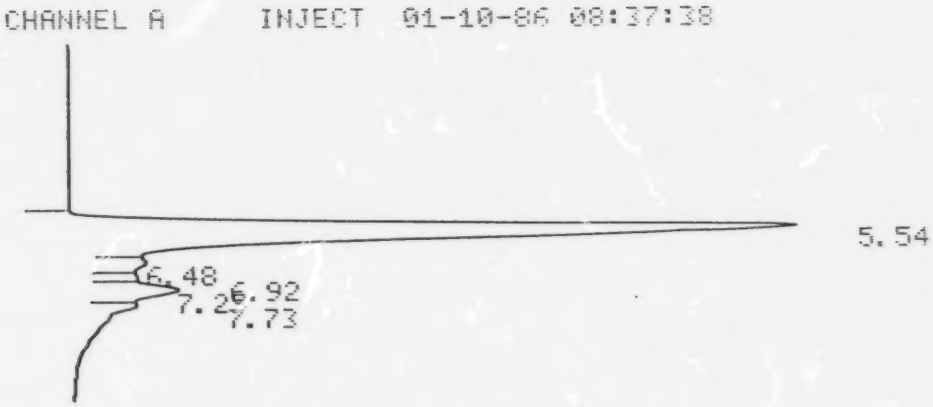


SYS 2 KEITHLY 23-09-86 10:27:32 CH= "A"

FILE 1. METHOD 0. RUN 82 INDEX 82

PEAK#	AREA%	RT	AREA BC
1	70.207	5.58	34145247 02
2	5.472	7.05	2661419 02
3	8.23	8.02	4002869 02
4	8.291	8.3	4032163 02
5	2.058	9.09	1001002 02
6	2.75	9.66	1337410 02
7	1.569	10.66	763237 02
8	1.423	11.72	691892 03
TOTAL	100.		48635239

Figure AS-7: Sample 284

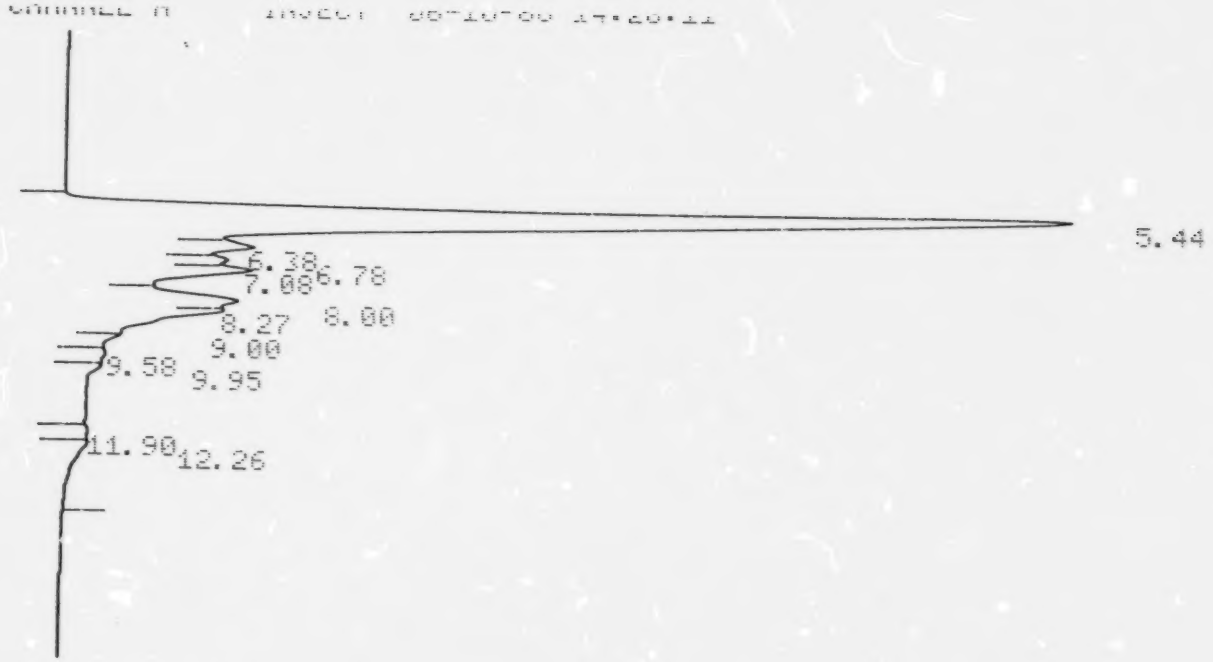


SYS 2 KEITHLY 01-10-86 08:37:38

FILE 1. METHOD 0. RUN 148 INDEX 148

PEAK#	AREA%	RT	AREA	BC
1	71.931	5.54	19019079	02
2	6.032	6.48	1594884	02
3	2.99	6.92	790487	02
4	9.49	7.29	2509193	02
5	9.558	7.73	2527147	03
TOTAL	100.		26440790	

Figure AS-8: Sample 3200

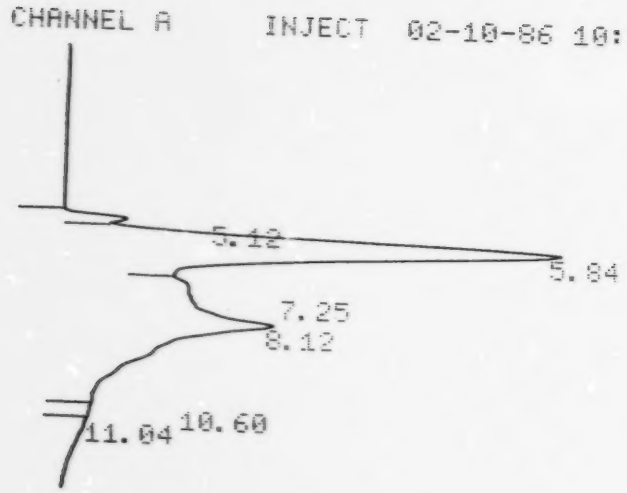


SYS 2 KEITHLY 06-10-86 14:26:11 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 227 INDEX 227

PEAK#	AREA%	RT	AREA	BC
1	54.449	5.44	27854638	02
2	7.38	6.38	3775628	02
3	4.228	6.78	2163175	02
4	7.983	7.08	4084096	02
5	8.145	8.	4166779	02
6	7.573	8.27	3874024	02
7	1.741	9.	890755	02
8	1.579	9.58	807766	02
9	4.269	9.95	2183961	02
10	0.926	11.9	473776	02
11	1.726	12.26	883151	03
TOTAL	100.		51157749	

Figure AS-9: Sample 3256

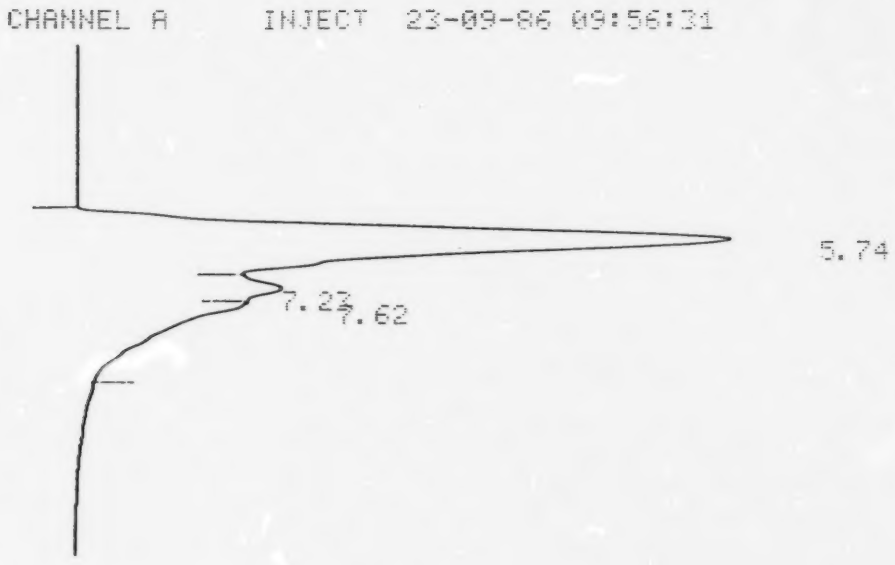


SYS 2 KEITHLY 02-10-86 10:51:49 CH=

FILE 1. METHOD 0. RUN 194 INDEX 194

PEAK#	AREA%	RT	AREA BC
1	1.795	5.12	692241 02
2	46.514	5.84	17935051 02
3	7.82	7.25	3015137 02
4	39.705	8.12	15309877 02
5	1.377	10.6	531142 02
6	2.788	11.04	1075143 03
TOTAL	100.		38558591

Figure AS-10: Sample 3259

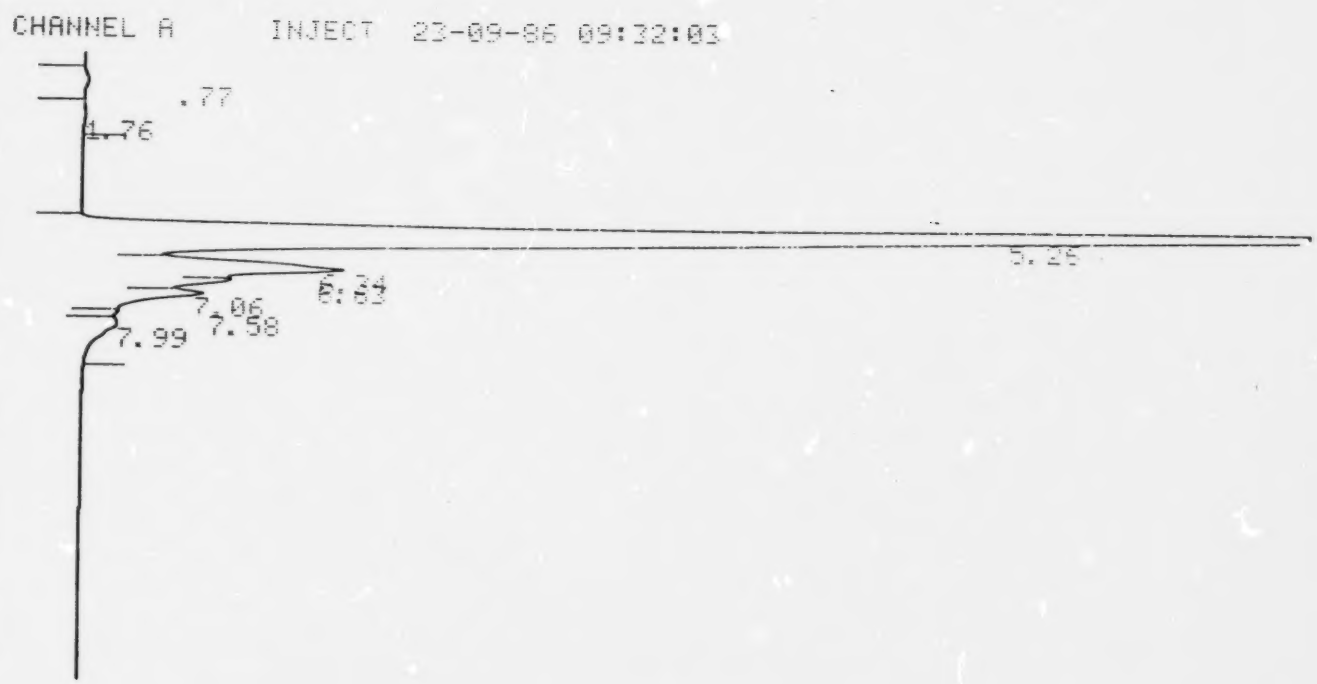


SYS 2 KEITHLY 23-09-86 09:56:31

FILE 1. METHOD 0. RUN 80 INDEX 80

PEAK#	AREA%	RT	AREA BC
1	68.85	5.74	30345802 02
2	14.851	7.23	6545564 02
3	16.299	7.62	7183779 03
TOTAL	100.		44075145

Figure AS-11: Sample LAD

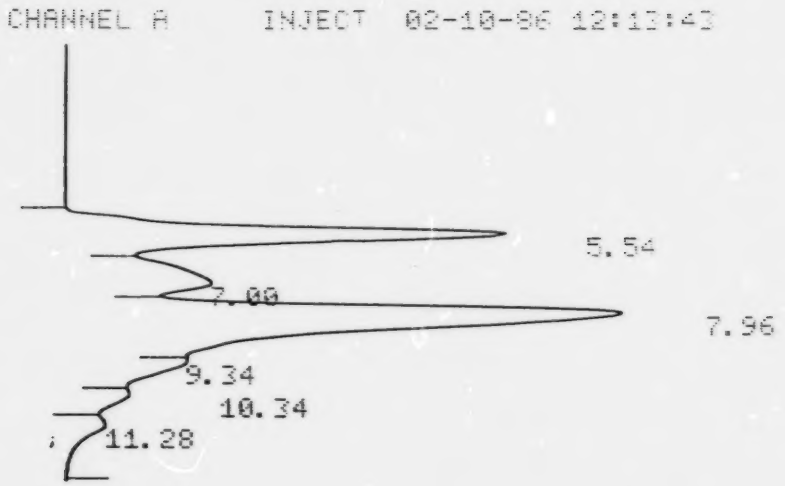


SYS 2 KEITHLY 23-09-86 09:32:03 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 79 INDEX 79

PEAK#	AREA%	RT	AREA BC
1	0.213	0.77	94588 02
2	0.133	1.76	58757 03
3	74.881	5.26	33196367 02
4	12.21	6.34	5413100 02
5	4.415	6.63	1957105 02
6	5.049	7.06	2238330 02
7	0.816	7.58	361872 02
8	2.282	7.99	1011759 03
TOTAL	100.		44331878

Figure AS-12: Sample HAD



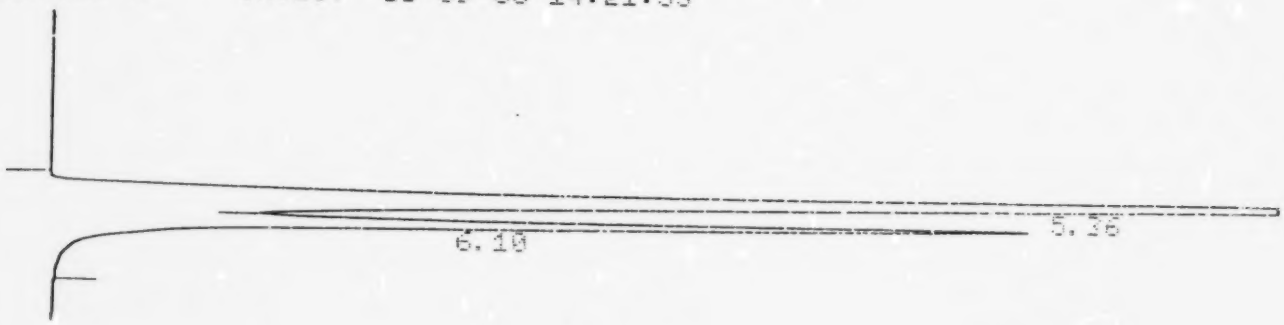
SYS 2 KEITHLY 02-10-86 12:13:43

FILE 1. METHOD 0. RUN 200 INDEX 200

PEAK#	AREA%	RT	AREA	BC
1	23.324	5.54	12005295	02
2	12.466	7.	6416493	02
3	49.724	7.96	25593935	02
4	8.004	9.34	4120083	02
5	3.715	10.34	1912311	02
6	2.767	11.28	1424184	03
TOTAL	100.		51472301	

Figure A5-13: Sample ST-3

CHANNEL A INJECT 23-09-86 14:21:55

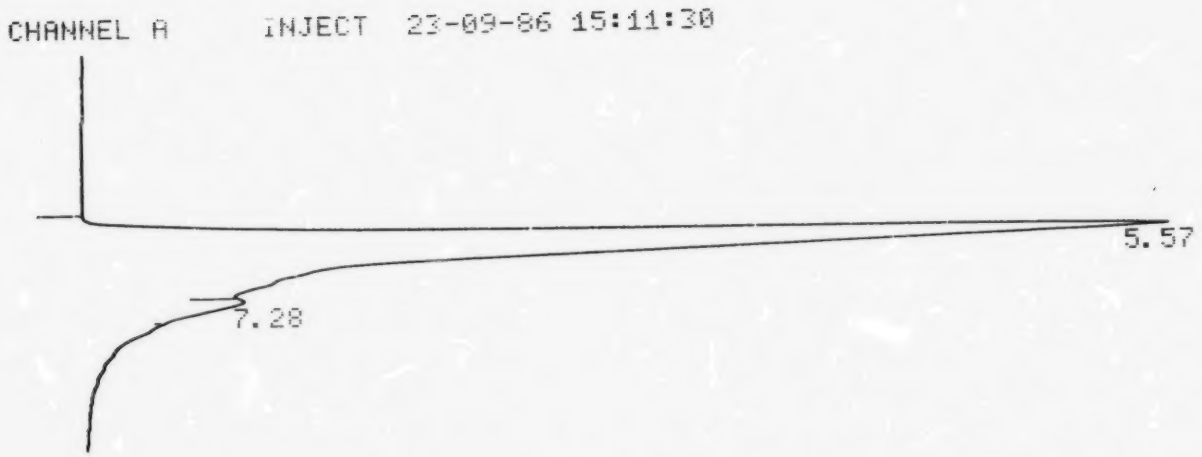


SYS 2 KEITHLY 23-09-86 14:21:55 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 99 INDEX 99

PEAK#	AREA%	RT	AREA	BC
1	67.813	5.36	28752165	02
2	32.187	6.1	13647178	03
TOTAL	100.		42399343	

Figure AS-14: Sample ST-4

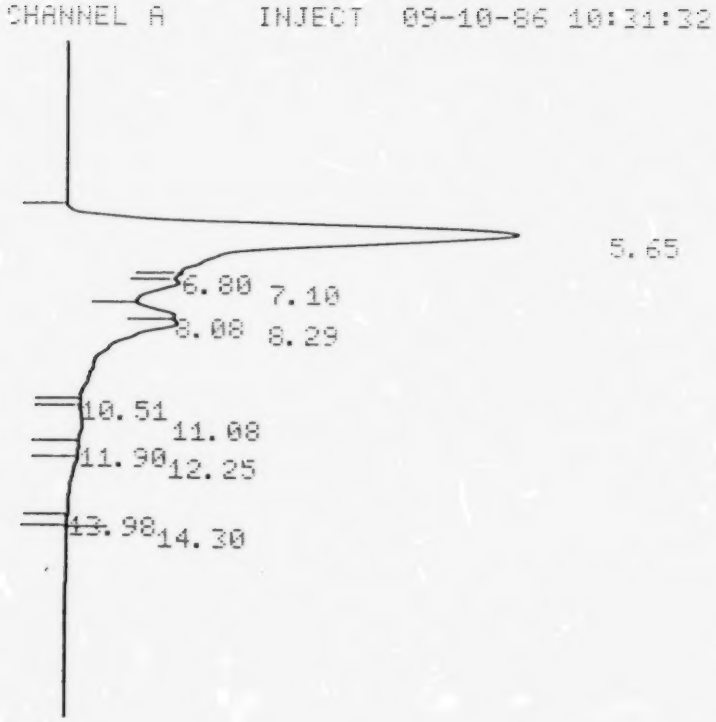


SYS 2 KEITHLY 23-09-86 15:11:30 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 104 INDEX 104

PEAK#	AREA%	RT	AREA BC
1	85.058	5.57	43847611 02
2	14.942	7.28	7702915 03
TOTAL	100.		51550526

Figure AS-15: Sample ST-6



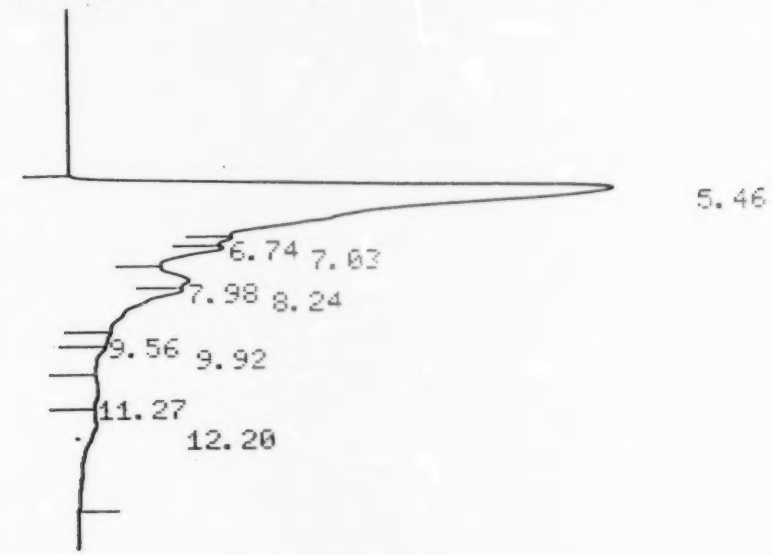
SYS 2 KEITHLY 09-10-86 10:31:32

FILE 1. METHOD 0. RUN 250 INDEX 250

PEAK#	AREA%	RT	AREA BC
1	60.279	5.65	18880537 02
2	3.232	6.8	1012180 02
3	9.6	7.1	3006942 02
4	6.765	8.08	2119039 02
5	15.613	8.29	4890180 02
6	0.394	10.51	123510 02
7	2.209	11.08	691805 02
8	0.817	11.9	255766 02
9	1.077	12.25	337384 02
10	0.015	13.98	4593 02
11	0.	14.3	29 03
TOTAL	100.		31321965

Figure AS-16: Sample ST-7

CHANNEL A INJECT 06-10-86 15:47:29

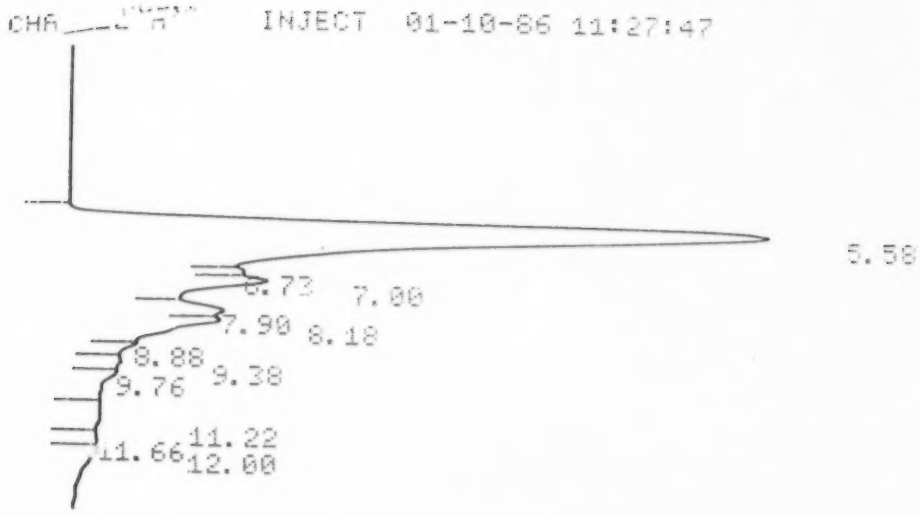


SYS 2 KEITHLY 06-10-86 15:47:29

FILE 1. METHOD 0. RUN 231 INDEX 231

PEAK#	AREA%	RT	AREA	BC
1	60.959	5.46	25244155	02
2	4.597	6.74	1903595	02
3	7.859	7.03	3254418	02
4	7.773	7.98	3218924	02
5	9.383	8.24	3885512	02
6	1.656	9.56	685670	02
7	2.197	9.92	909798	02
8	2.514	11.27	1040988	02
9	3.064	12.2	1268662	03
TOTAL	100.		41411722	

Figure AS-17: Sample ST-8



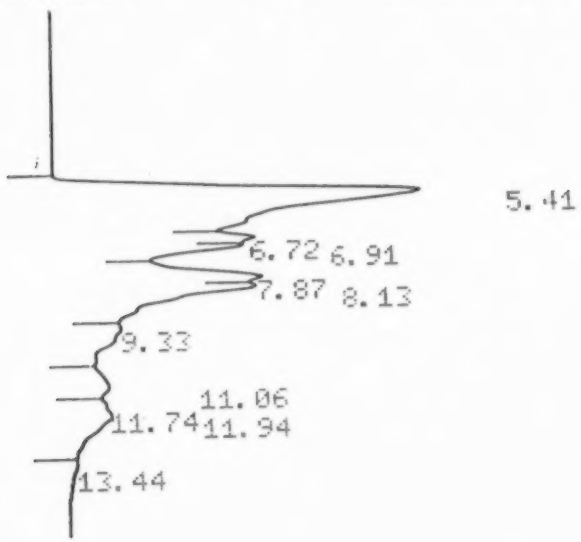
SYS 2 KEITHLY 01-10-86 11:27:47

FILE 1. METHOD 0. RUN 160 INDEX 160

PEAK#	AREA%	RT	AREA BC
1	58.245	5.58	28877489 02
2	3.937	6.73	1951794 02
3	10.688	7.	5299296 02
4	6.534	7.9	3239374 02
5	8.124	8.18	4028067 02
6	2.092	8.88	1037029 02
7	1.99	9.38	986633 02
8	2.883	9.76	1429502 02
9	2.533	11.22	1255732 02
10	1.015	11.66	503197 02
11	1.96	12.	971617 03
TOTAL	100.		49579730

Figure AS-18: Sample ST-10

CHANNEL A INJECT 01-10-86 12:00:54

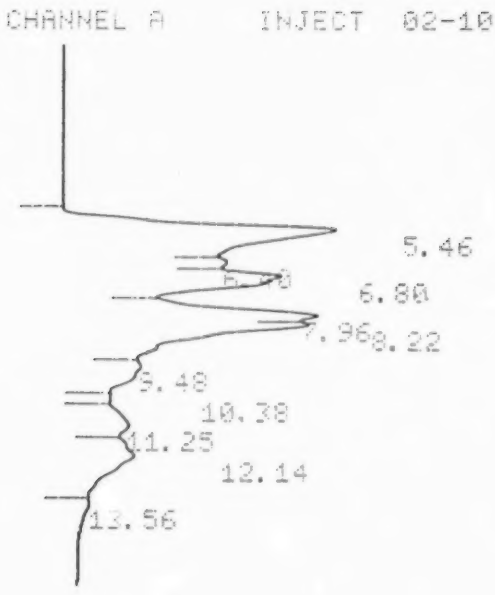


SYS 2 KEITHLY 01-10-86 12:00:54

FILE 1. METHOD 0. RUN 162 INDEX 162

PEAK#	AREA%	RT	AREA	BC
1	40.379	5.41	16930372	02
2	7.117	6.72	2984088	02
3	7.754	6.91	3251206	02
4	11.406	7.87	4782434	02
5	14.576	8.13	6111469	02
6	6.846	9.33	2870577	02
7	4.485	11.06	1880280	02
8	1.736	11.74	728046	02
9	4.653	11.94	1950723	02
10	1.047	13.44	439179	03
TOTAL	100.		41928374	

Figure A5-19: Sample ST-11

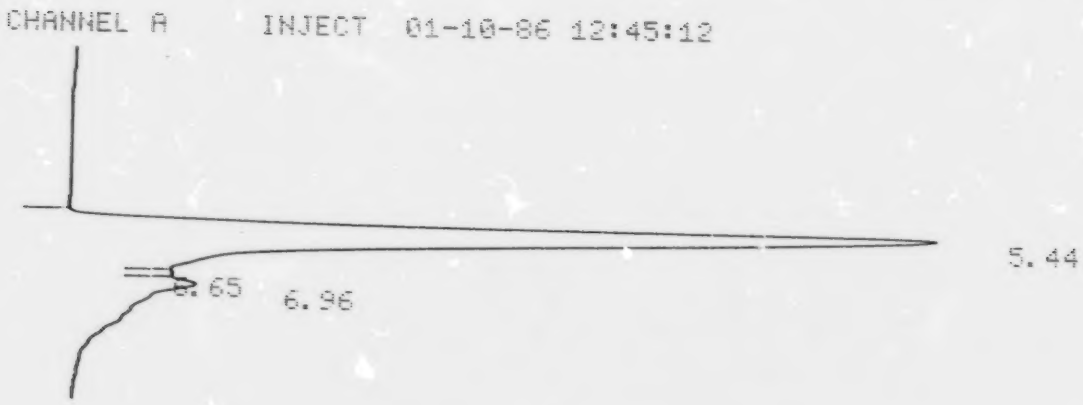


SYS 2 KEITHLY 02-10-86 10:13:01

FILE 1. METHOD 0. RUN 192 INDEX 192

PEAK#	AREA%	RT	AREA BC
1	23.978	5.46	10278110 02
2	5.861	6.4	2512347 02
3	15.996	6.8	6856862 02
4	13.687	7.96	5866975 02
5	17.072	8.22	7318029 02
6	6.794	9.48	2912224 02
7	1.423	10.38	609987 02
8	5.602	11.25	2401227 02
9	8.104	12.14	3473905 02
10	1.482	13.56	635360 03
TOTAL	100.		42865026

Figure AS-20: Sample ST-12

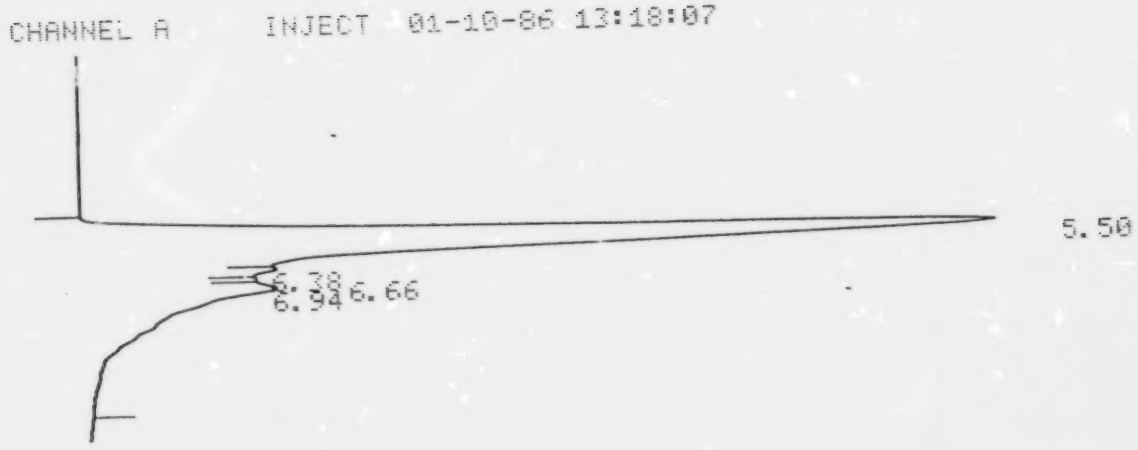


SYS 2 KEITHLY 01-10-86 12:45:12 CH= "A"

FILE 1. METHOD 0. RUN 165 INDEX 165

PEAK#	AREA%	RT	AREA BC
1	78.608	5.44	27453034 02
2	2.824	6.65	986371 02
3	18.568	6.96	6484725 03
TOTAL	100.		34924130

Figure A5-21: Sample ST-14



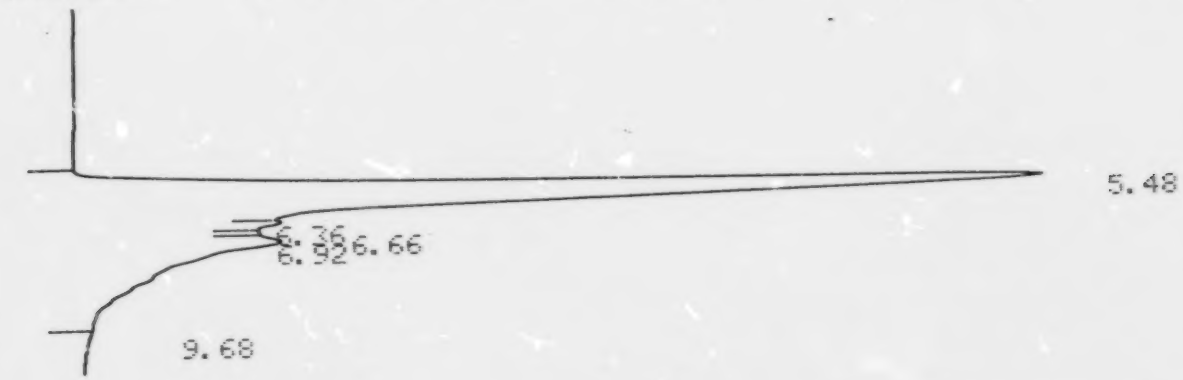
SYS 2 KEITHLY 01-10-86 13:18:07 CH= "A" PS=

FILE 1. METHOD 0. RUN 168 INDEX 168

PEAK#	AREA%	RT	AREA BC
1	68.232	5.5	29189097 02
2	5.78	6.38	2472502 02
3	2.762	6.66	1181543 02
4	23.227	6.94	9936272 03
TOTAL	100.		42779414

Figure AS-22: Sample ST-21

CHANNEL A INJECT 01-10-86 13:42:29



SVS 2 KEITHLY 01-10-86 13:42:29 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 170 INDEX 170

PEAK#	AREA%	RT	AREA	BC
1	68.005	5.48	30407552	02
2	5.837	6.36	2609819	02
3	2.79	6.66	1247426	02
4	22.836	6.92	10211014	02
5	0.532	9.68	238083	03
TOTAL	100.		44713894	

APPENDIX 6

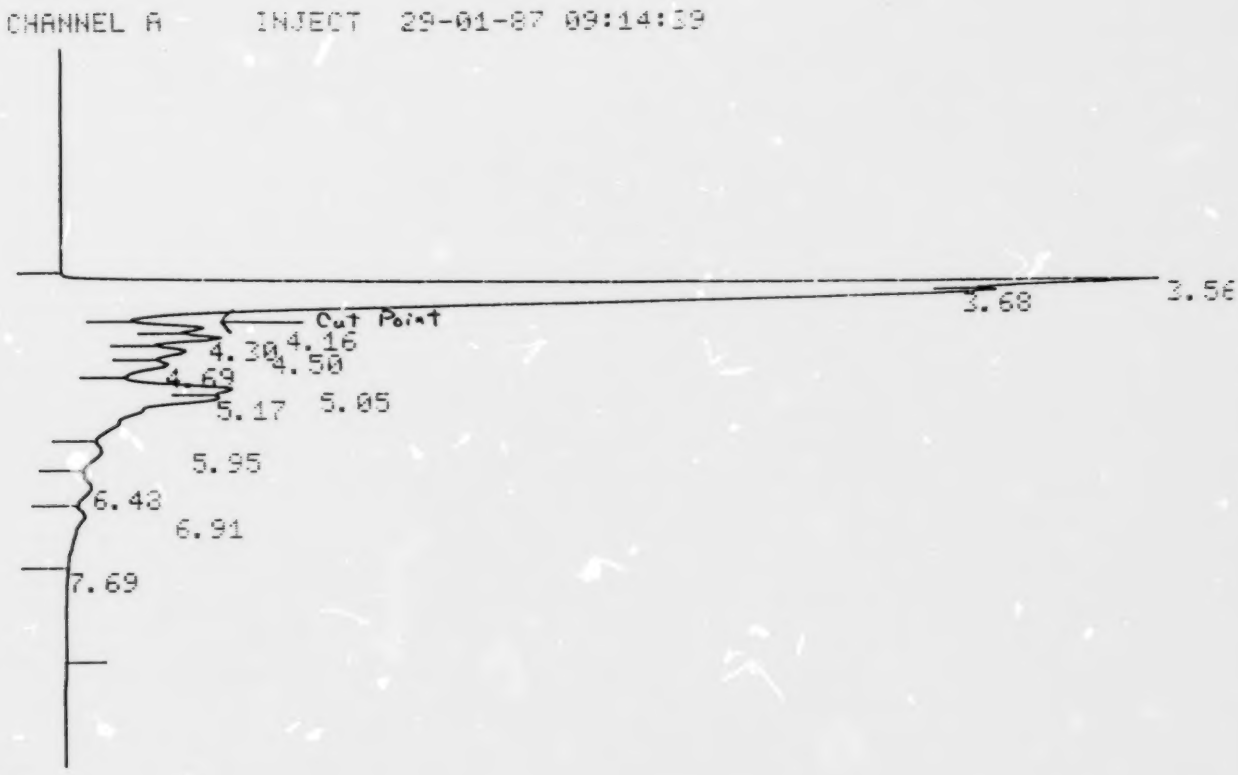
SFC Results of Each Analysis of Middle Distillates at 3600 psi and 90°C

Sample	Wt% Aromatics	Mean	Std Dev	%RSD
8	31.7, 33.0	32.3	0.9	2.8
102	28.8, 28.8	28.8	0.0	0.0
103	34.1, 33.5, 32.9	33.5	0.6	1.8
185	36.2, 38.3, 39.0, 38.7, 39.2	38.3	1.2	3.3
187	27.5, 30.2, 32.4, 29.0, 27.4, 28.9, 30.0, 30.1, 29.1	29.4	1.5	5.1
281	30.2, 29.8	30.0	0.3	1.0
284	29.2, 28.9, 28.0	28.7	0.6	2.1
3200	46.2, 45.9, 45.7	45.9	0.3	0.7
3256	52.8, 52.9, 52.5	52.7	0.2	0.4
3259	31.7, 31.7	31.7	0.0	0.0
LAD	26.0, 25.1	25.6	0.6	2.3
HAD	77.8, 77.6, 77.7, 77.7	77.7	0.1	0.1
ST-3	32.7, 31.9, 32.7, 32.8	32.5	0.4	1.2
ST-4	14.9, 15.1	15.0	0.1	0.7
ST-6	40.6, 40.4	40.5	0.1	0.3
ST-7	39.8, 40.3, 37.6	39.2	1.4	3.6
ST-8	42.7, 42.7, 42.3, 42.5	42.6	0.2	0.5
ST-10	60.6, 60.4	60.5	0.1	0.2
ST-11	77.3, 76.6	77.0	0.5	0.7
ST-12	22.1, 21.8, 21.4	21.8	0.4	1.8
ST-14	32.3, 32.4	32.4	0.1	0.3
ST-21	32.5, 30.4, 32.2	31.7	1.1	3.5

APPENDIX 7

SFC Chromatograms of All Middle Distillate Samples at 3600 psi and 35°C

Figure A7-1 : Sample 8

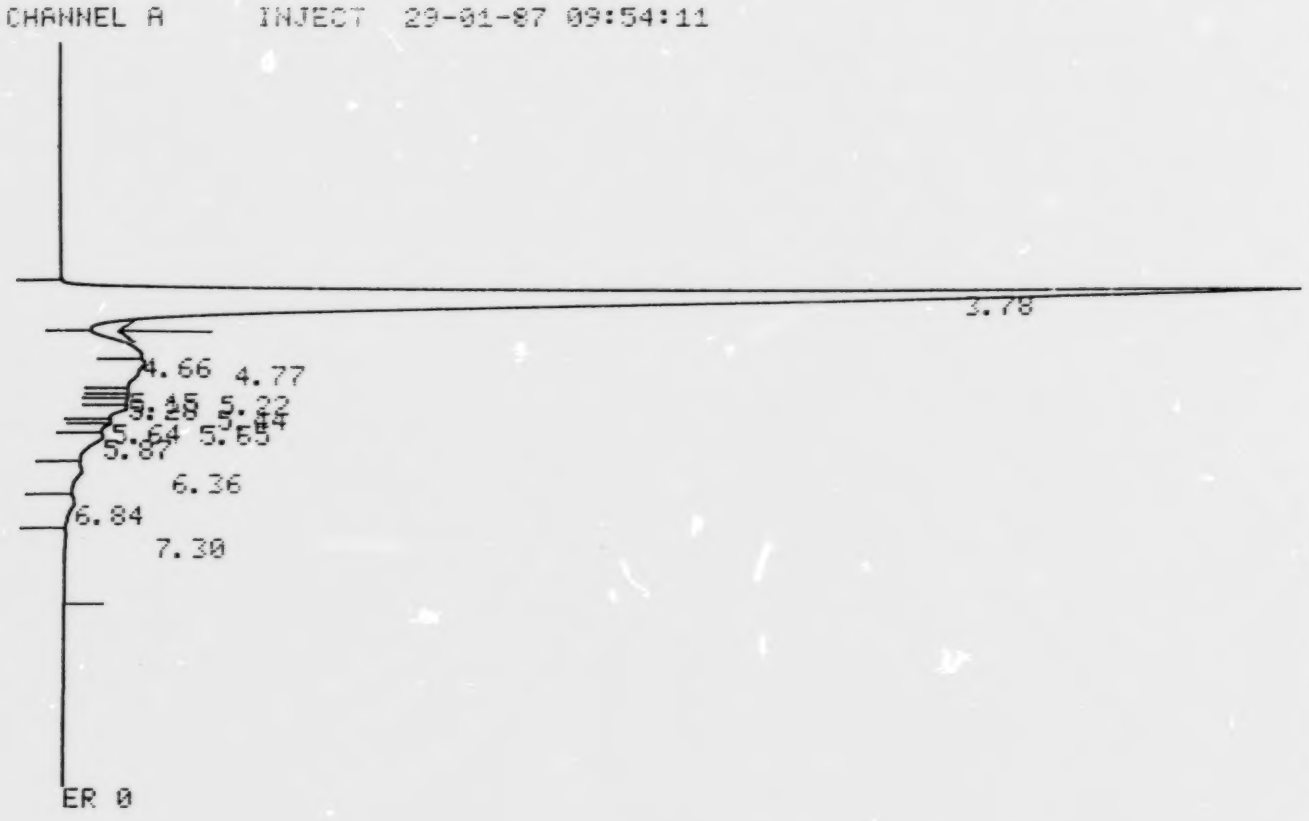


SYS 2 PACKED COL 29-01-87 09:14:39 CH= "A" PS= 1

FILE 1. METHOD 0. RUN 181 INDEX 181

PEAK#	AREA%	RT	AREA BC
1	28.459	3.56	7213046 02
2	32.007	3.68	8112165 02
3	3.936	4.16	997573 02
4	4.339	4.3	1099794 02
5	4.392	4.5	1113271 02
6	4.209	4.69	1066724 02
7	6.199	5.05	1571212 02
8	9.71	5.17	2460994 02
9	2.457	5.95	622838 02
10	2.13	6.48	539792 02
11	1.855	6.91	470177 02
12	0.306	7.69	77532 03
TOTAL	100.		25345118

Figure A7-2 : Sample 102

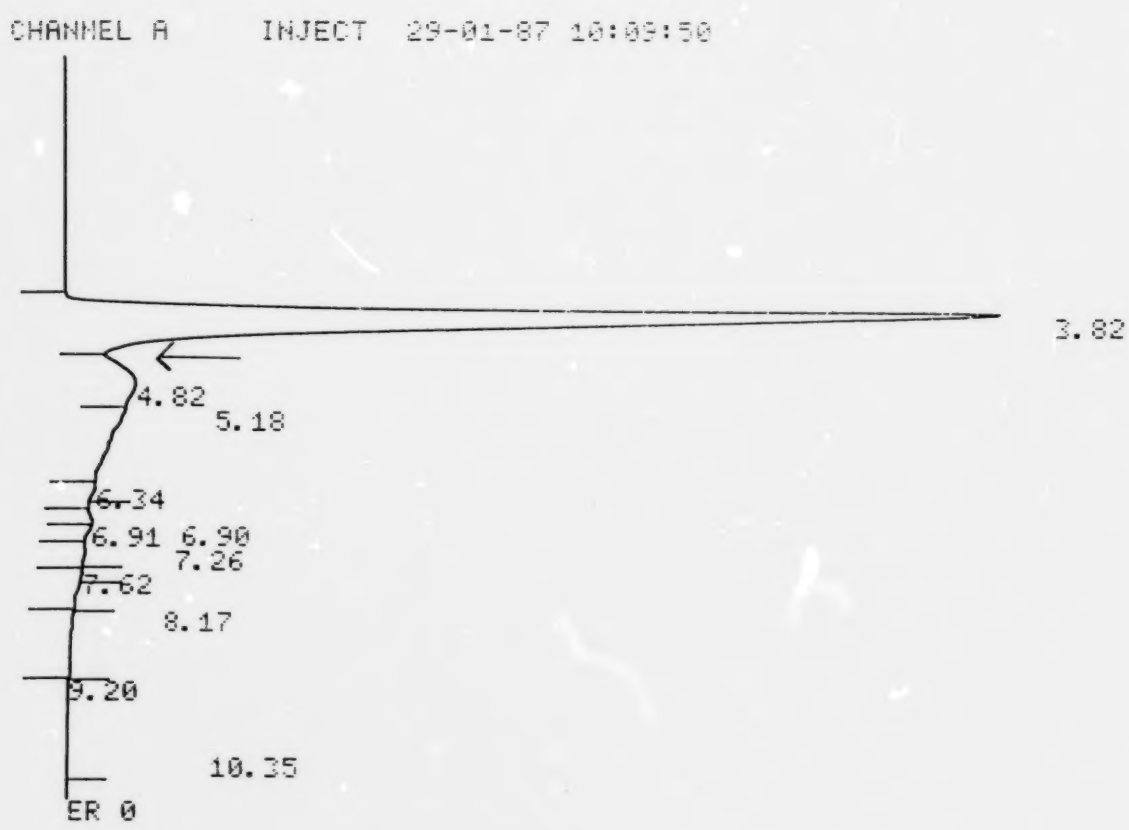


SYS 2 PACKED COL 29-01-87 09:54:11 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 184 INDEX 184

PEAK#	AREA%	RT	AREA	BC
1	70.1	3.78	13145593	02
2	6.22	4.66	1166504	02
3	8.487	4.77	1591547	02
4	1.234	5.15	231336	02
5	0.947	5.22	177497	02
6	1.86	5.28	348752	02
7	3.045	5.44	571033	02
8	0.731	5.64	137049	02
9	1.592	5.65	298628	02
10	3.007	5.87	563893	02
11	1.679	6.36	314874	02
12	0.878	6.84	164575	02
13	0.22	7.3	41336	03
TOTAL	100.		18752617	

Figure A7-3 : Sample 103

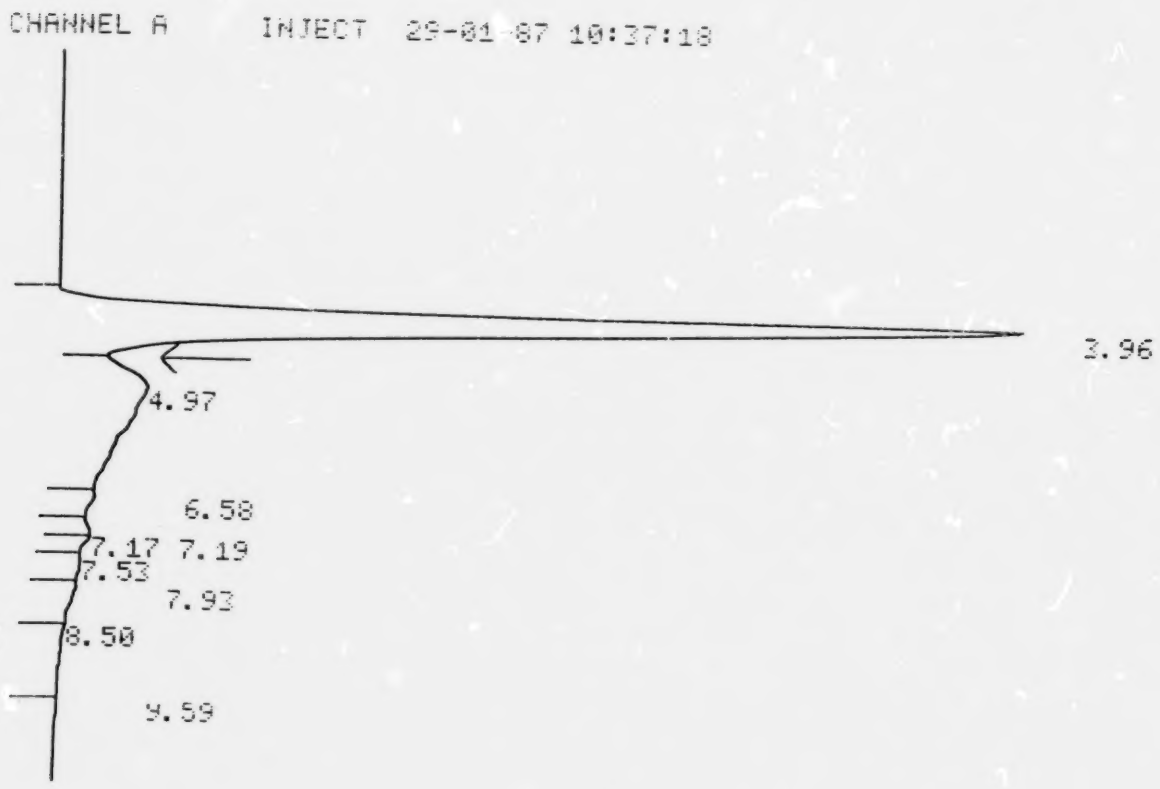


SYS 2 PACKED COL 29-01-87 10:09:50 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 185 INDEX 185

PEAK#	AREA%	RT	AREA BC
1	65.803	3.82	12524017 02
2	11.778	4.82	2241658 02
3	21.827	5.18	4154180 08
4	0.11	6.34	21007 05
5	0.179	6.9	34059 06
6	0.186	6.91	35432 06
7	0.08	7.26	15227 07
8	0.037	7.62	7072 05
9	0.	8.17	23 05
10	0.	9.2	22 05
TOTAL	100.		19032697

Figure A7-4 : Sample 185

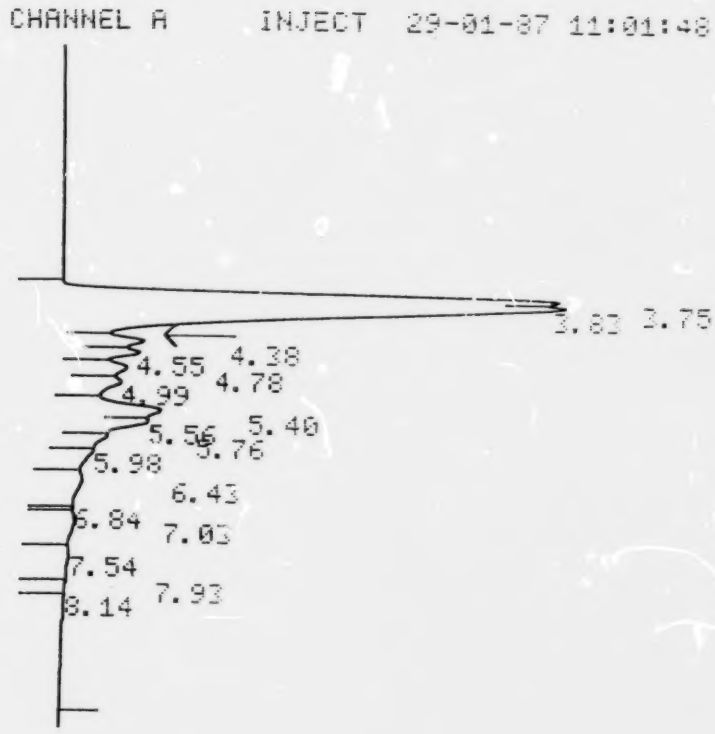


SYS 2 PACKED COL 29-01-87 10:37:18 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 187 INDEX 187

PEAK#	AREA%	RT	AREA BC
1	63.429	3.96	15140269 02
2	25.424	4.97	6068676 02
3	2.667	6.58	636540 02
4	1.67	7.17	398577 02
5	1.483	7.19	354103 02
6	1.934	7.53	461667 02
7	1.995	7.93	476147 02
8	1.135	8.5	271019 02
9	0.263	9.59	62707 03
TOTAL	100.		23869705

Figure A7-5 : Sample 187

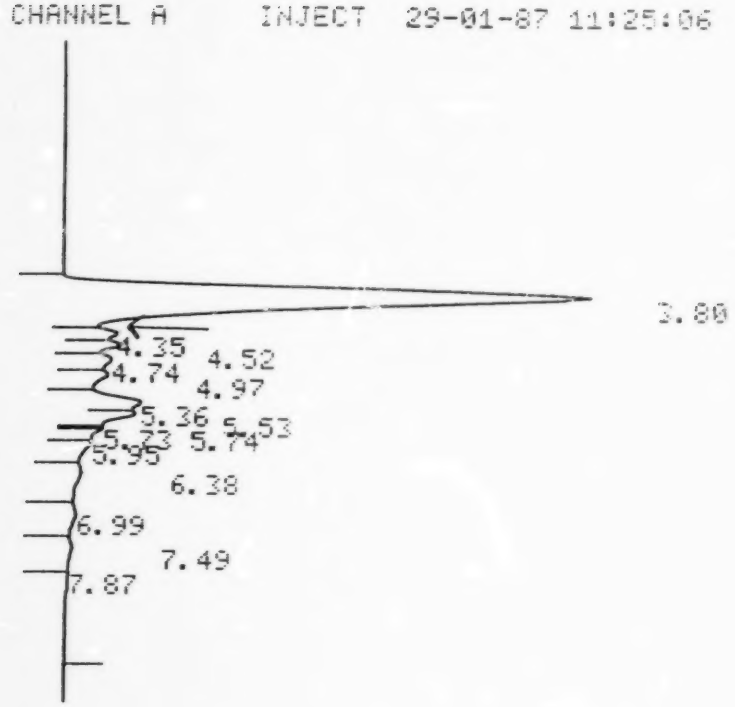


SYS 2 PACKED COL 29-01-87 11:01:48

FILE 1. METHOD 0. RUN 189 INDEX 189

PEAK#	AREA%	RT	AREA BC
1	19.176	3.75	2922473 02
2	39.216	3.83	5976538 02
3	4.423	4.38	674076 02
4	3.837	4.55	584709 02
5	4.466	4.78	680647 02
6	4.58	4.99	698055 02
7	7.475	5.4	1139188 02
8	4.953	5.56	754852 02
9	2.684	5.76	409120 02
10	2.533	5.98	386016 02
11	2.791	6.43	425277 02
12	0.151	6.84	22997 02
13	1.764	7.03	268851 02
14	1.058	7.54	161300 02
15	0.267	7.93	40685 02
16	0.625	8.14	95306 03
TOTAL	100.		15240090

Figure A7-6 : Sample 281

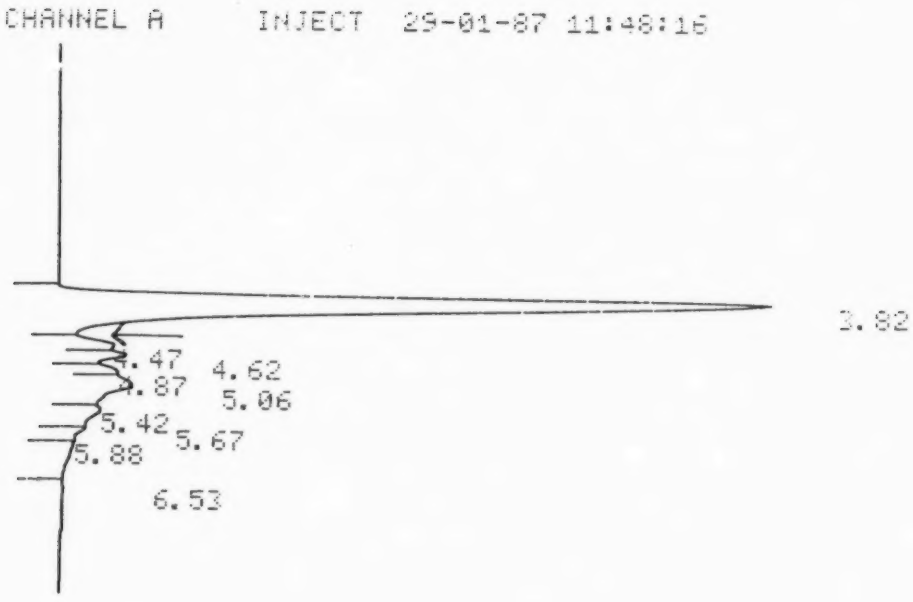


SYS 2 PACKED COL 29-01-87 11:25:06

FILE 1. METHOD 0. RUN 191 INDEX 191

PEAK#	AREA%	RT	AREA BC
1	61.883	3.8	7771186 02
2	3.333	4.35	418544 02
3	3.538	4.52	444291 02
4	4.017	4.74	504505 02
5	4.048	4.97	508347 02
6	6.691	5.36	840259 02
7	5.003	5.53	628273 02
8	0.542	5.73	68101 02
9	2.154	5.74	270440 02
10	2.662	5.95	334308 02
11	2.783	6.38	349521 02
12	1.646	6.99	206738 02
13	1.109	7.49	139273 02
14	0.59	7.87	74063 03
TOTAL	100.		12557849

Figure A7-7 : Sample 284

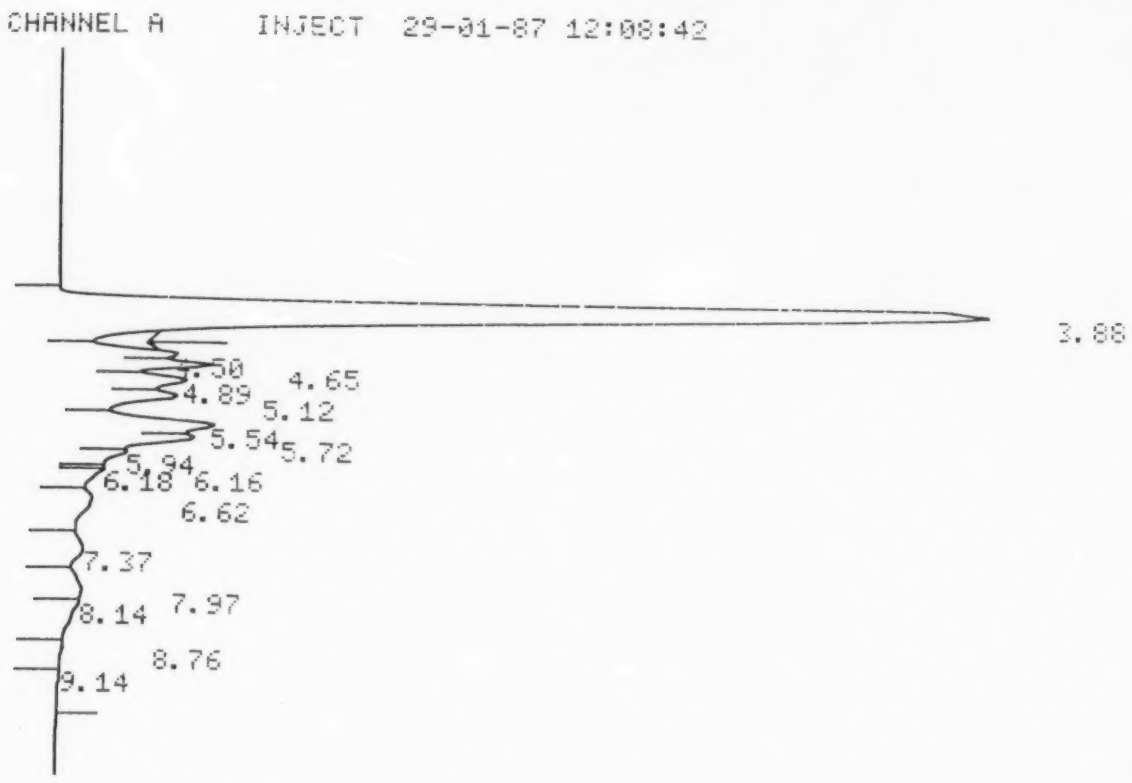


SYS 2 PACKED COL 29-01-87 11:48:16

FILE 1. METHOD 0. RUN 193 INDEX 193

PEAK#	AREA%	RT	AREA BC
1	70.163	3.82	8564210 02
2	3.436	4.47	419456 02
3	4.31	4.62	526038 02
4	3.136	4.87	382821 02
5	10.016	5.06	1222549 02
6	4.331	5.42	528589 02
7	1.564	5.67	190942 02
8	2.017	5.88	246155 02
9	1.028	6.53	125422 03
TOTAL	100.		12206182

Figure A7-8 : Sample 3200

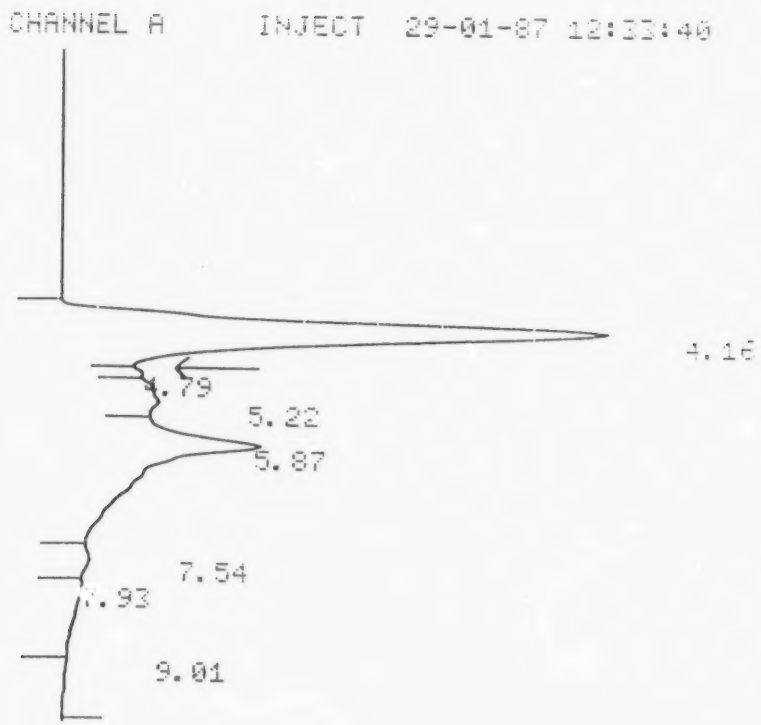


SYS 2 PACKED COL 29-01-87 12:08:42 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 195 INDEX 195

PEAK#	AREA%	RT	AREA	BC
1	54.242	3.88	13262347	02
2	3.798	4.5	928524	02
3	4.723	4.65	1154764	02
4	5.35	4.89	1308143	02
5	5.41	5.12	1322843	02
6	7.151	5.54	1748533	02
7	5.087	5.72	1243878	02
8	2.555	5.94	624687	02
9	0.481	6.16	117523	02
10	2.036	6.18	497831	02
11	3.195	6.62	781217	02
12	2.139	7.37	523039	02
13	1.858	7.97	454394	02
14	1.548	8.14	378562	02
15	0.347	8.76	84950	02
16	0.078	9.14	19182	03
TOTAL	100.		24450417	

Figure A7-9 : Sample 3256

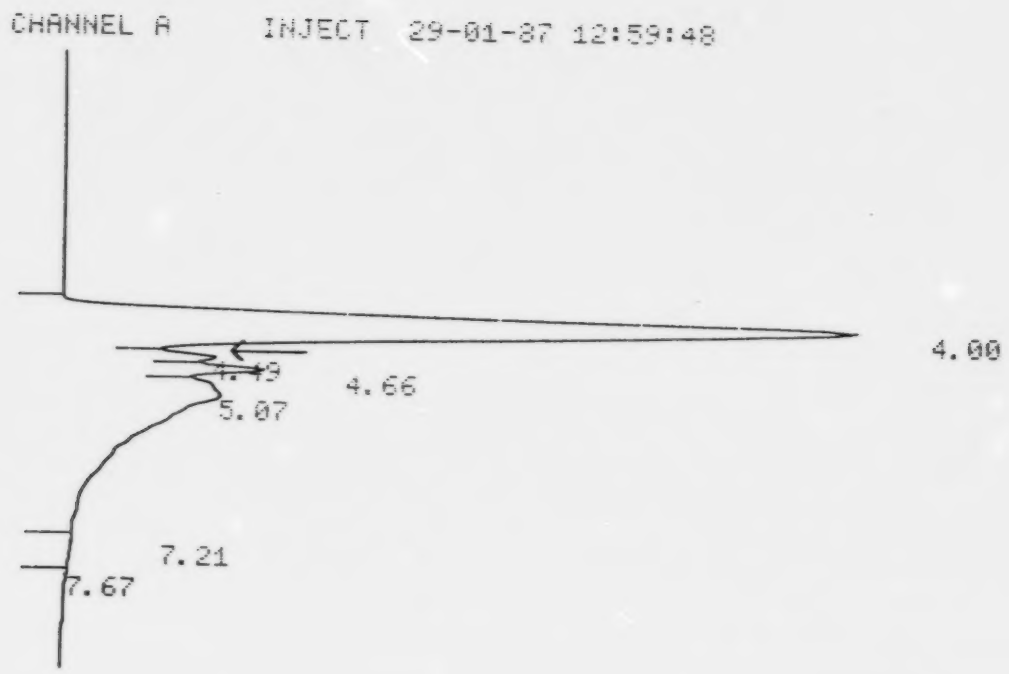


SYS 2 PACKED COL 29-01-87 12:33:40

FILE 1. METHOD 0. RUN 197 INDEX 197

PEAK#	AREA%	RT	AREA BC
1	46.055	4.16	10199675 02
2	2.836	4.79	627995 02
3	11.246	5.22	2490677 02
4	33.863	5.87	7499534 02
5	2.689	7.54	595492 02
6	3.019	7.93	668512 02
7	0.293	9.01	64906 01
TOTAL	100.		22146791

Figure A7-10 : Sample 3259

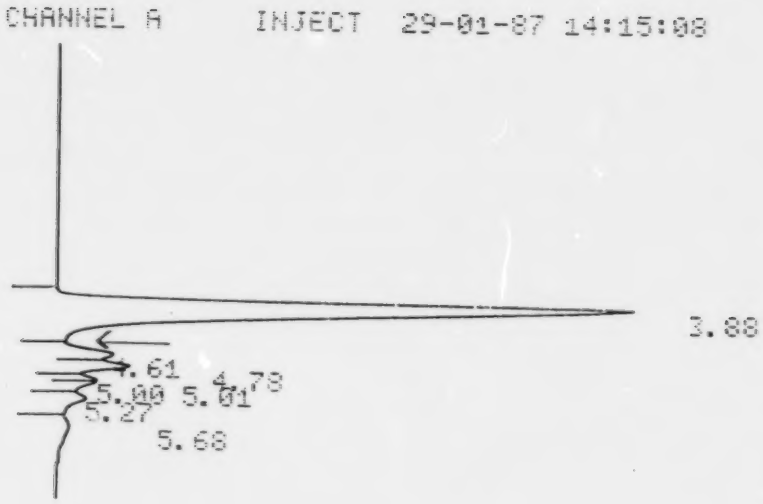


SYS 2 PACKED COL 29-01-87 12:59:48 CH= "A"

FILE 1. METHOD 0. RUN 199 INDEX 199

PEAK#	AREA%	RT	AREA BC
1	54.755	4.	12867796 02
2	5.039	4.49	1184105 02
3	7.456	4.66	1752104 02
4	31.348	5.07	7367051 02
5	0.823	7.21	193477 02
6	0.58	7.67	136275 03
TOTAL	100.		23500808

Figure A7-11 : Sample LAD

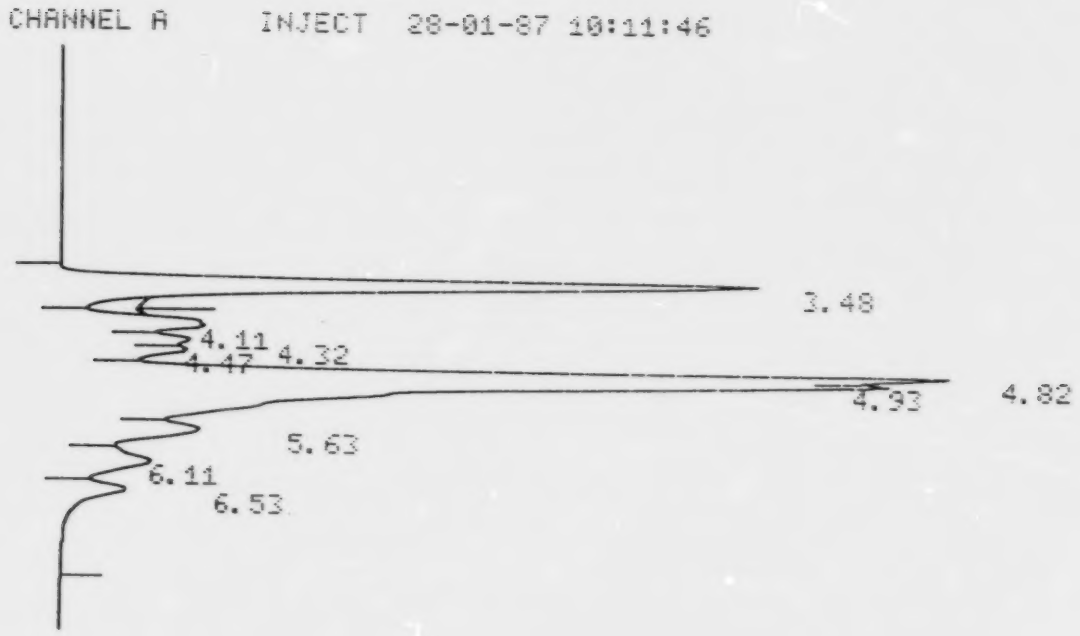


SVS 2 PACKED COL 29-01-87 14:15:08

FILE 1. METHOD 0. RUN 205 INDEX 205

PEAK#	AREA%	RT	AREA BC
1	76.08	3.88	6107822 02
2	5.742	4.61	460991 02
3	6.584	4.78	528569 02
4	2.057	5.	165151 02
5	2.684	5.01	215498 02
6	3.722	5.27	298817 02
7	3.131	5.68	251341 03
TOTAL	100.		8028189

Figure A7-12 : Sample HAD

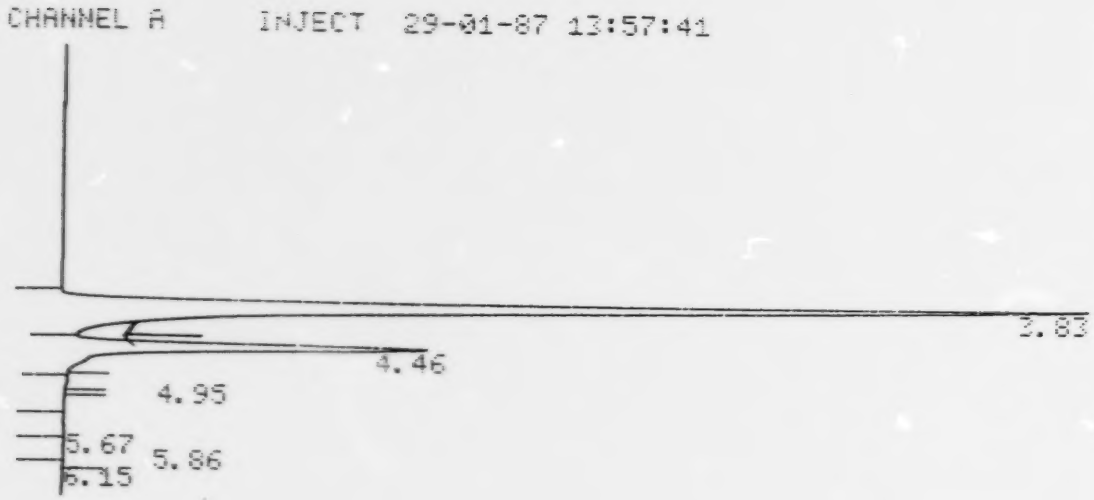


SYS 2 PACKED COL 28-01-87 10:11:46 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 155 INDEX 155

PEAK#	AREA%	RT	AREA BC
1	20.7_	3.48	6327593 02
2	5.434	4.11	1661085 02
3	3.509	4.32	1072580 02
4	3.763	4.47	1150386 02
5	20.921	4.82	6395346 02
6	31.274	4.93	9560154 02
7	6.465	5.63	1976166 02
8	4.803	6.11	1468198 02
9	3.132	6.53	957284 03
TOTAL	100.		30568792

Figure A7-13 : Sample ST-3

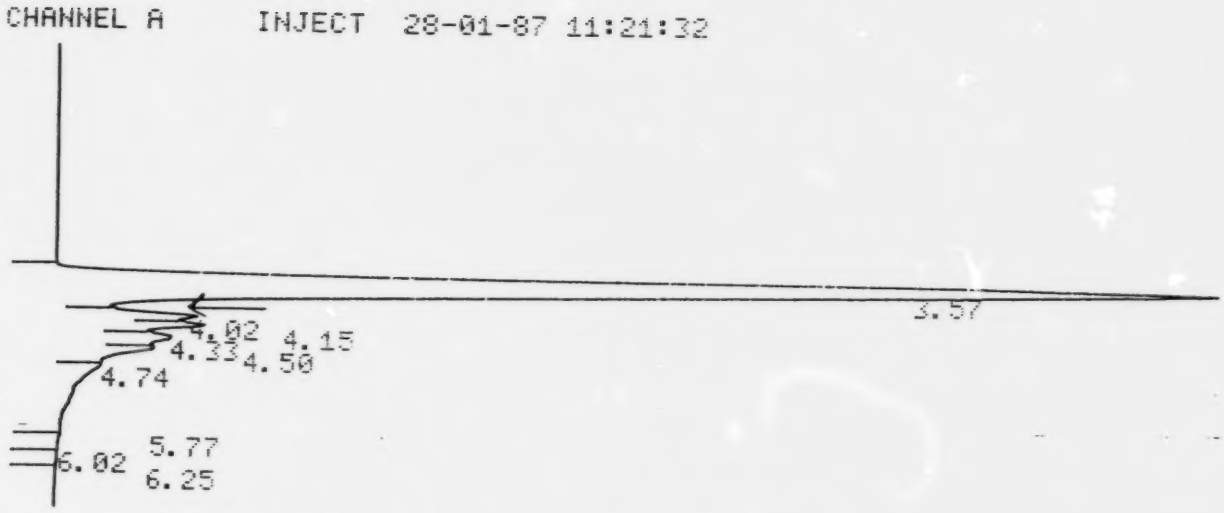


SYS 2 PACKED COL 29-01-87 13:57:41 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 203 INDEX 203

PEAK#	AREA%	RT	AREA BC
1	77.302	3.83	7443583 08
2	22.377	4.46	2154706 05
3	0.064	4.95	6181 05
4	0.138	5.67	13303 02
5	0.115	5.86	11069 02
6	0.003	6.15	324 03
TOTAL	100.		9629166

Figure A7-14 : Sample ST-4

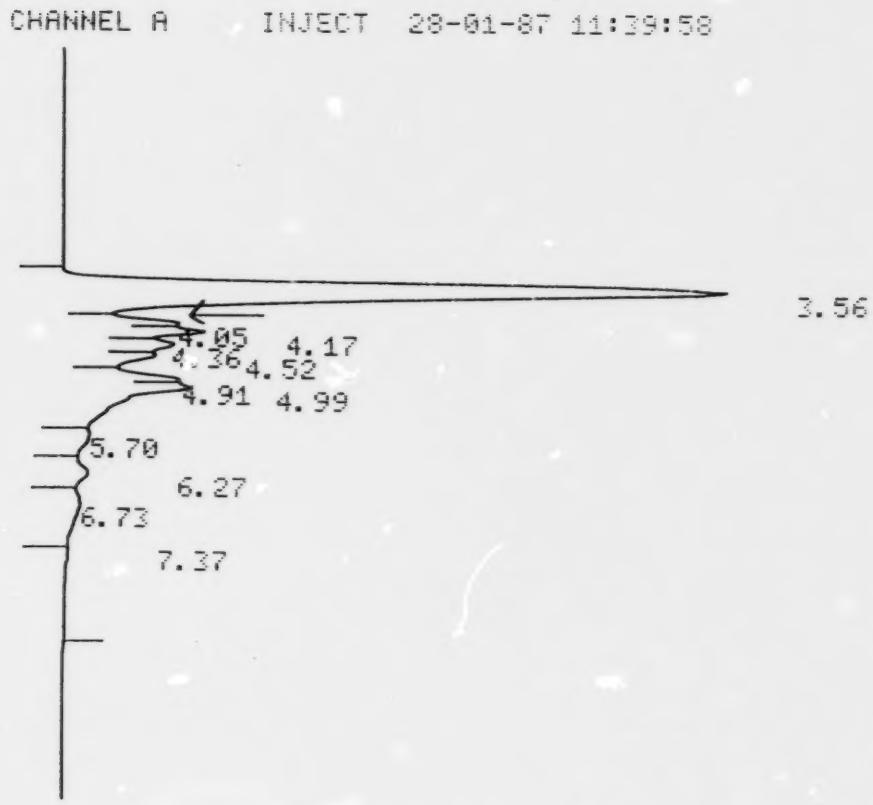


SYS 2 PACKED COL 28-01-87 11:21:32 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 162 INDEX 162

PEAK#	AREA%	RT	AREA BC
1	72.867	3.57	13429439 02
2	5.275	4.02	972149 02
3	5.247	4.15	966976 02
4	5.696	4.33	1049875 02
5	5.18	4.5	954755 02
6	5.157	4.74	950514 02
7	0.279	5.77	51409 02
8	0.161	6.02	29689 02
9	0.138	6.25	25379 03
TOTAL	100.		18430185

Figure A7-15 : Sample ST-6

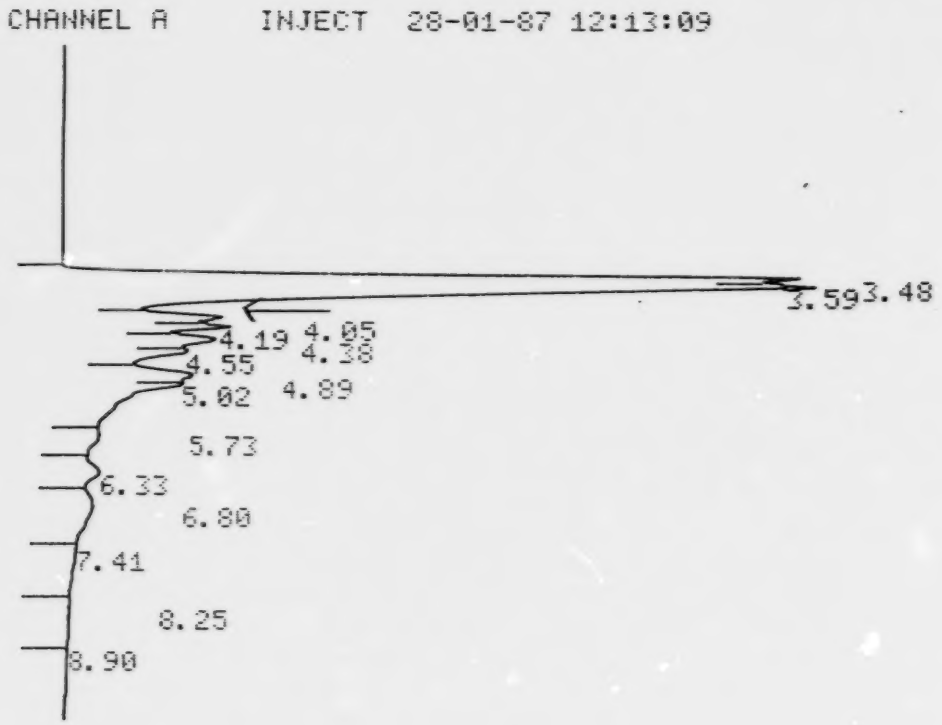


SYS 2 PACKED COL 28-01-87 11:39:58

FILE 1. METHOD 0. RUN 164 INDEX 164

PEAK#	AREA%	RT	AREA BC
1	51.252	3.56	8400223 02
2	4.43	4.05	726120 02
3	6.298	4.17	1032178 02
4	6.094	4.36	998866 02
5	5.271	4.52	863924 02
6	5.336	4.91	874574 02
7	12.706	4.99	2082492 02
8	2.644	5.7	433345 02
9	2.547	6.27	417394 02
10	2.863	6.73	469282 02
11	0.559	7.37	91600 03
TOTAL	100.		16389998

Figure A7-16 : Sample ST-7

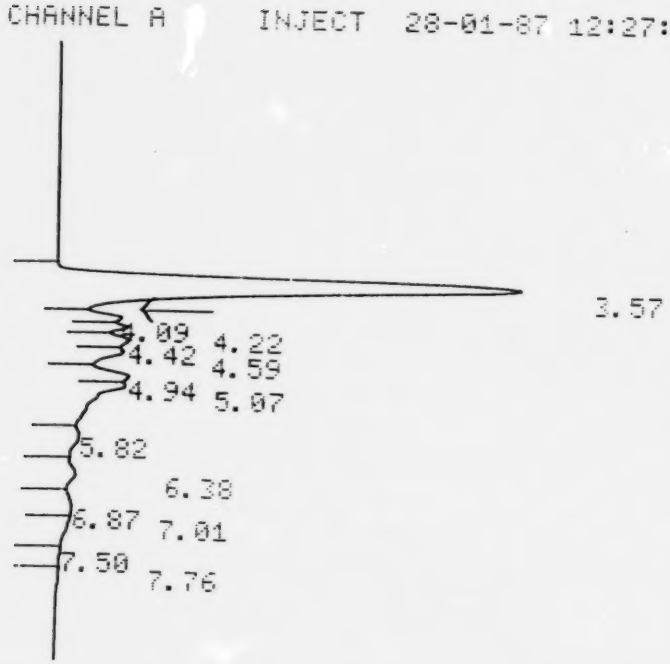


SYS 2 PACKED COL 28-01-87 12:13:09 CH= "A"

FILE 1. METHOD 0. RUN 167 INDEX 167

PEAK#	AREA%	RT	AREA BC
1	17.207	3.48	3820085 02
2	34.234	3.59	7600278 02
3	5.059	4.05	1123054 02
4	4.814	4.19	1068859 02
5	6.259	4.38	1389510 02
6	5.206	4.55	1155712 02
7	5.939	4.89	1318505 02
8	9.085	5.02	2016982 02
9	2.707	5.73	600977 02
10	2.984	6.33	662588 02
11	3.912	6.8	868472 02
12	1.442	7.41	320112 02
13	0.762	8.25	169105 02
14	0.391	8.9	86844 03
TOTAL	100.		22201183

Figure A7-17 : Sample ST-8

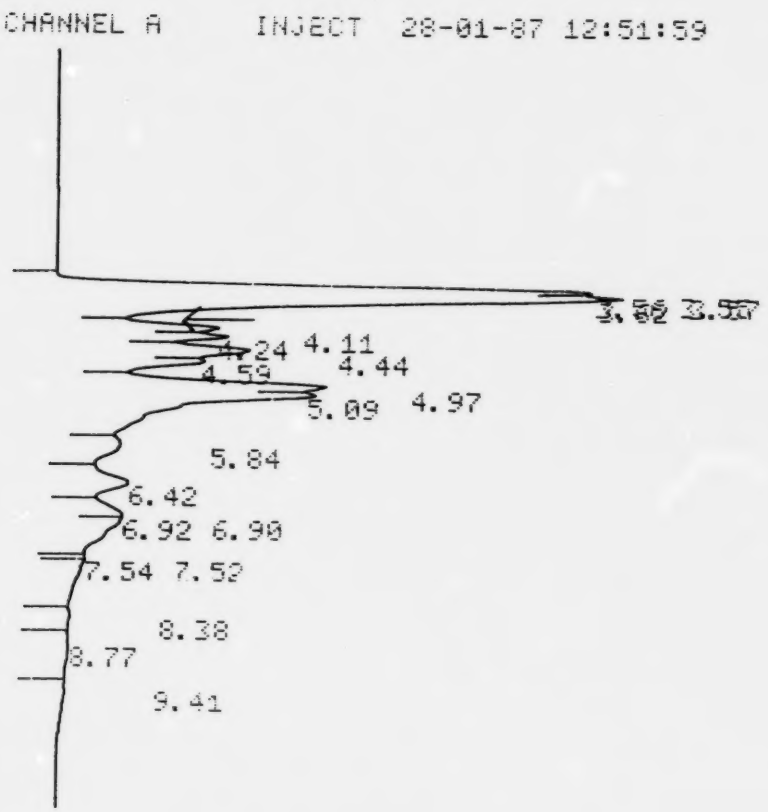


SYS 2 PACKED COL 28-01-87 12:27:09

FILE 1. METHOD 0. RUN 168 INDEX 168

PEAK#	AREA%	RT	AREA BC
1	50.479	3.57	5740757 02
2	4.072	4.09	463093 02
3	4.154	4.22	472393 02
4	5.933	4.42	674753 02
5	5.914	4.59	672537 02
6	6.076	4.94	691042 02
7	10.719	5.07	1218988 02
8	3.702	5.82	420978 02
9	3.092	6.38	351673 02
10	2.408	6.87	273813 02
11	1.922	7.01	218582 02
12	0.632	7.5	71906 02
13	0.898	7.76	102098 02
TOTAL	100.		11372613

Figure A7-18 : Sample ST-10



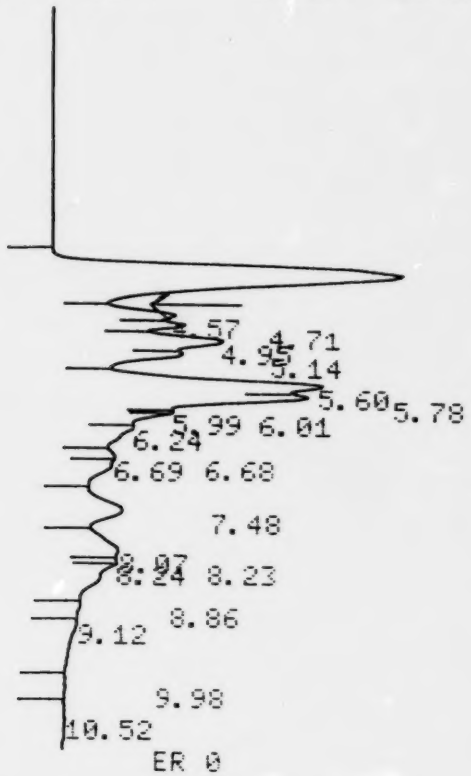
SYS 2 PACKED COL 28-01-87 12:51:59

FILE 1. METHOD 0. RUN 170 INDEX 170

PEAK#	AREA%	RT	AREA BC
1	8.951	3.55	2298052 02
2	0.649	3.56	168504 02
3	0.643	3.57	166934 02
4	21.687	3.62	5630722 02
5	4.491	4.11	1166013 02
6	4.08	4.24	1059328 02
7	7.031	4.44	1825602 02
8	4.684	4.59	1216194 02
9	9.018	4.97	2341329 02
10	15.269	5.09	3964555 02
11	4.31	5.84	1119028 02
12	5.014	6.42	1301870 02
13	2.794	6.9	725390 02
14	4.965	6.92	1289132 02
15	0.369	7.52	95774 02
16	2.674	7.54	694362 02
17	0.814	8.38	211311 02
18	1.479	8.77	384140 02
19	1.178	9.41	305939 03
TOTAL	100.		25964179

Figure A7-19 : Sample ST-11

CHANNEL A INJECT 29-01-87 13:32:05

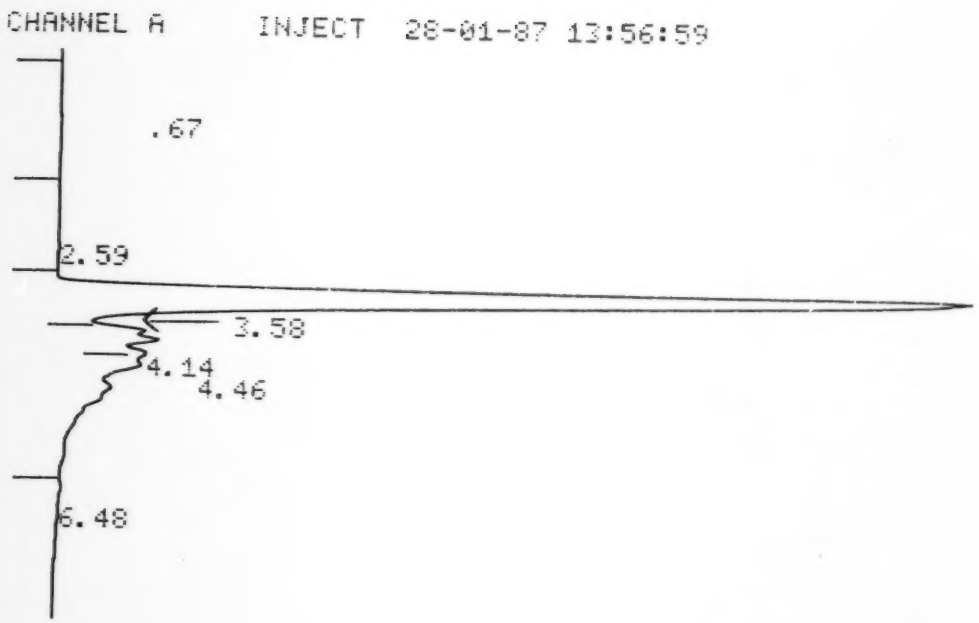


SYS 2 PACKED COL 29-01-87 13:32:05

FILE 1. METHOD 0. RUN 201 INDEX 201

PEAK#	AREA%	RT	AREA BC
1	24.468	3.97	5945010 02
2	4.474	4.57	1087055 02
3	3.798	4.71	922847 02
4	7.623	4.95	1852276 02
5	5.081	5.14	1234603 02
6	12.153	5.6	2952925 02
7	9.82	5.78	2385896 02
8	0.929	5.99	225637 02
9	3.435	6.01	834663 02
10	4.57	6.24	1110448 02
11	1.637	6.68	397763 02
12	3.707	6.69	900658 02
13	5.764	7.48	1400610 02
14	4.153	8.07	1009040 02
15	0.877	8.23	213012 02
16	4.159	8.24	1010596 02
17	1.016	8.86	246835 02
18	1.613	9.12	391909 02
19	0.336	9.98	81716 02
20	0.386	10.52	93871 03
TOTAL	100.		24297370

Figure A7-20 : Sample ST-12

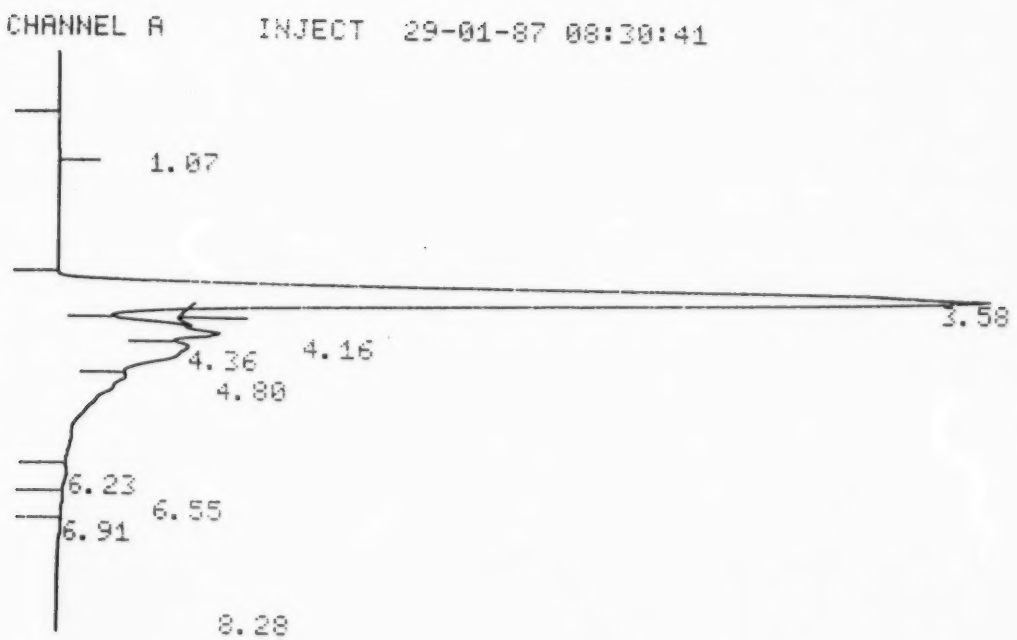


SYS 2 PACKED COL 28-01-87 13:56:59 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 175 INDEX 175

PEAK#	AREA%	RT	AREA BC
1	0.104	0.67	16690 02
2	0.089	2.59	14344 02
3	69.257	3.58	11126542 02
4	10.081	4.14	1619563 02
5	19.002	4.46	3052820 02
6	1.467	6.48	235629 03
TOTAL	100.		16065538

Figure A7-21 : Sample ST-14

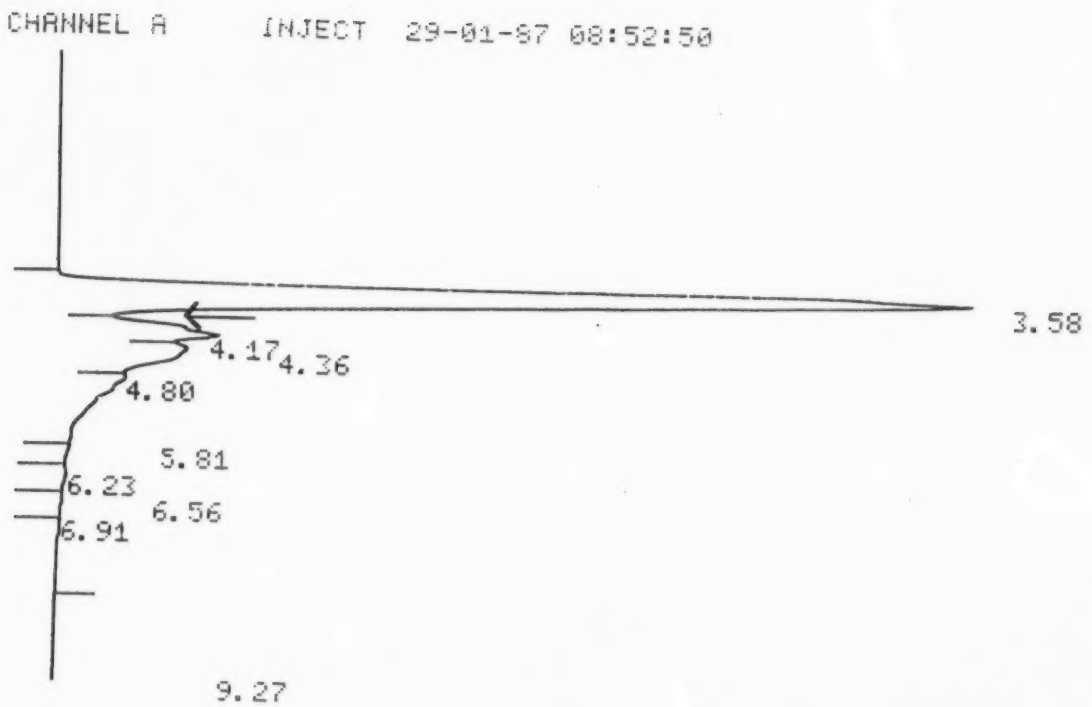


SYS 2 PACKED COL 29-01-87 08:30:41 CH= "A"

FILE 1. METHOD 0. RUN 177 INDEX 177

PEAK#	AREA%	RT	AREA BC
1	0.014	1.07	2671 01
2	63.323	3.58	11666273 02
3	11.151	4.16	2054432 02
4	13.224	4.36	2436296 02
5	10.353	4.8	1907387 02
6	0.845	6.23	155591 02
7	0.535	6.55	98506 02
8	0.555	6.91	102249 03
TOTAL	100.		18423405

Figure A7-22 : Sample ST-21



SYS 2 PACKED COL 29-01-87 08:52:50 CH= "A"

FILE 1. METHOD 0. RUN 179 INDEX 179

PEAK#	AREA%	RT	AREA BC
1	63.365	3.58	11455256 02
2	11.247	4.17	2033214 02
3	13.278	4.36	2400491 02
4	9.598	4.8	1735098 02
5	0.802	5.81	144970 02
6	0.814	6.23	147152 02
7	0.503	6.56	90891 02
8	0.394	6.91	71272 03
TOTAL	100.		18078344

APPENDIX 8

SFC Results of Each Analysis of Middle Distillates at 3600 psi and 35°C

Sample	Wt% Aromatics	Mean	Std Dev	%RSD
8	40.3, 40.3	40.3	0.0	0.0
102	30.7, 30.7	30.7	0.0	0.0
103	35.1, 34.1	34.6	0.7	2.0
185	37.4, 36.9	37.1	0.4	1.1
187	43.0, 42.9	42.9	0.1	0.2
281	39.7, 38.5	39.1	0.9	2.3
284	31.1, 29.7	30.4	1.0	3.3
3200	46.7, 46.9	46.8	0.1	0.2
3256	55.2, 55.3	55.2	0.1	0.2
3259	46.2, 46.7	46.4	0.4	0.9
LAD	25.5, 25.4	25.4	0.1	0.4
HAD	80.6, 81.0	80.8	0.3	0.4
ST-3	23.9, 23.8	23.8	0.1	0.4
ST-4	29.0, 27.9	28.4	0.8	2.8
ST-6	50.3, 50.1	50.2	0.1	0.2
ST-7	49.4, 49.7	49.5	0.2	0.4
ST-8	51.8, 51.6	51.7	0.1	0.2
ST-10	69.5, 69.8	69.6	0.2	0.3
ST-11	79.2, 78.9, 77.1, 76.8	78.0	1.2	1.5
ST-12	32.0, 31.7, 32.2	32.0	0.3	0.4
ST-14	37.7, 37.6	37.6	0.1	0.3
ST-21	37.7, 37.7	37.7	0.0	0.0

APPENDIX 9

Repeatability of Absolute Area Measurements for Several Diesel and Middle Distillate Samples

(Silica column, 90°C, 3250 psi)

Sample		Absolute Area	Relative Area (%)
HAD		50649585	75.6
		51589921	76.6
		49598846	75.5
		49164171	77.4
		28056898 *	77.5
		50167780	77.5
		27634793	77.3
	RSD:	25.0%	1.2%
		1.9% *	
3256		30887711	49.2
		29433300	49.5
		20368255	45.7
		22867268	46.3
		9180229 *	43.4
		17271294	46.9
		25102900	49.4
		25724428	47.7
	RSD:	31.8%	4.5%
		17.5% *	
284		11979031	22.2
		11283344	21.5
		11156317	21.5
		12253672	22.6
		13544534	22.7
		12764437	23.5
		10567964	21.1
		10623310	21.0
		11203081	20.9
		9546026	21.4
		6182375 *	20.9
		9549726	21.1
	RSD:	17.5%	4.4%
		11.1% *	

* Points marked with an asterisk were excluded from the calculation of RSD.

APPENDIX 10

Example Calculation of Sample Recovery from SFC Data

Sample 284 (diluted 1:10 in CS_2)

Area counts of saturates = 39,262,505

Saturates response factor (from calibration curve) = 642,900 $\mu g^{-1} \cdot \mu L$

Conc of saturates $= \frac{39,262,505}{642,900}$

$= 61.07\ \mu g/\mu L$

Area counts of aromatics = 11,062,526

Aromatics response factor = 613,800 $\mu g^{-1} \cdot \mu L$

Conc of aromatics $= \frac{11,062,526}{613,800}$

$= 18.02\ \mu g/\mu L$

Total conc(diluted sample) = 79.09 $\mu g/\mu L$

Total conc before dilution = 790.0 $\mu g/\mu L$

Density of sample = 826.2 $\mu g/\mu L$

$\therefore$ Recovery $= \frac{790.9}{826.2} \times 100$

$= 95.7\%$